Squaramide and bis-urea supramolecular gels

By

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Abstract

In the field of supramolecular chemistry, supramolecular low molecular weight gelators (LMWG) have attracted the public attention. Supramolecular gel is a very attractive soft materials formed by non-covalent interactions. The frameworks based on non-covalent interactions give the supramolecular gels the most important properties in dynamics and reversibility. Dynamic characters provide a variety of characterisation methods and reversibility enables them to heal structures in respond of external stimuli such as light, heat and so on. This project can be divided into two main parts. At first, gel screening and characterization have done for squaramides **2.1**-**2.8** which came from the Dr Rob Elmes cooperative laboratory in Maynooth University. Half of the squaramaides were gelators, and one of them was metallogelator which gelled selected solvents together with copper chlorides and nitrates. In order to characterize the physical properties of gels, rheology has been carried out. Secondly, analogues **2.9**-**2.12** have been synthesised. After that, gel screening and characterisation proceeded for isoniazid and nicotinic hydrazide terminated gelators with both meta-disbstituted aryl linker and tetraethyl diphenylmethane linker **2.9**-**2.12**. All compands have been analysed by Nuclear Magnetic Resonance (NMR), Mass spectroscopy (MS) and elemental analysis. Analogues **2.9** and **2.11** were found to be good metallogelators in the presence of copper and cadmium chlorides. Gelator **2.10** was able to give a list of partial gels while **2.12** was found to be a non-gelator. The crystals obtained from the gel screen process were send for the single crystal diffraction in order to find out the structure. What is more, typical gels formed from each gelator were charicterised by rheology.

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List of Abbreviation

ACN	Acetonitrile
ACO	Acetone
AFM	Atomic force microscopy
CGC	Critical gelation concentration
d	Doublet
1,2-DCB	1,2-Dichlorobenzene
1,2-DBE	1,2-Dibromoethane
dd	Double doublet
ddd	Double double doublet
DA reaction	Diels Alder reaction
DMAP	4-(Dimethylamino)pyridine
DMF	Dimethylformamide
DPPA	Diphenyl phosphoryl azide
FT-IR	Fourier transform infra-red
G	Gel
IS	Insoluble
m	Multiplet
Mw	Molecule weight
NMR	Nuclear magnetic resonance
PG	Partial gel
ppm	Parts per million
PXRD	Powder X-ray diffraction
q	Quartet
s	Singlet
S	Soluble
SEM	Scanning electron microscopy
T	Triplet
1,2,4-TCB	1,2,4-Trichlorobenzene

td	Triple doublet
TEM	Transmission electron microscopy
TG	Transparent gel
*T*gel	Critical gelation temperature
UV-vis	Ultraviolet–visible spectroscopy
V	Volume
XRD	X-ray diffraction

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1 Introduction

1.1 Supramolecular chemistry

One-dimensional nanostructured materials have been attracting increasing attention due to their unique optical, electronic and chemical properties. These materials are constructed using supramolecular chemistry which is concerned with network structures established through non-covalent bonds. These intermolecular bonds include ion-ion interactions, ion-dipole interactions, dipole-dipole interactions, cation- and anion-π interactions, van der Waals' forces, hydrogen bonding, π- π stacking interactions and closed shell interactions.[1] Self-assembly is an important characteristic of the supramolecular structures, which can potentially be used in the area of materials to help reduce the repairing or replacing cost.[2] Additionally, this kind of ability has been found to form soft materials such as gels, with applications in drug crystallisation as a medium, [3] for drug delivery, [4] in sensors[5] and as in antibacterial gels. [6]

1.1.1 Ion-ion interactions

Ion-ion interaction is the strongest non-covalent interaction whose energy is 100-350 kJ·mol^{-1}, and can be comparable to the strength of covalent bonds. A common example is sodium chloride. In one sodium chloride cubic lattice, a Na^+ cation is coordinated to six Cl^- anions. [1] (**Figure 1**)

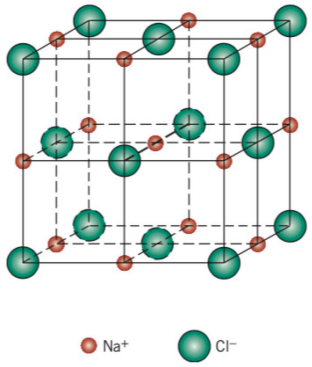
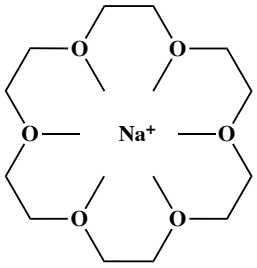


Figure 1. Example of NaCl unit cell for ion-ion interactions.[7]

1.1.2 Ion-dipole interactions

These interactions exist between ions and polar molecules. The strength of this kind of bond is 50-200 kJ·mol^{-1}, which comes up to the second, only lower than ion-ion interactions. Crown ether complex with alkali metal ions (**Scheme 1**) are linked by such ion dipole interactions. In

the structure shown below in **Scheme 1**, the O atoms in the macrocyclic ether plays the role of polar molecules. The lone pair electrons on each O atom is attracted by the Na^+ cation.



Scheme 1. The structure of Na^+ crown ether complex.

1.1.3 Dipole-dipole interactions

Dipole-dipole interactions have energies in the range of 5-50 $kJ \cdot mol^{-1}$ and are responsible for the interactions between polar moles. In polar compounds such as ketones there are two different types of dipolar interaction[1] (**Figure 2**). When one dipole aligns with another, there would be distinct attractive interactions formed between dipoles due to the discrepancy of electrical properties.

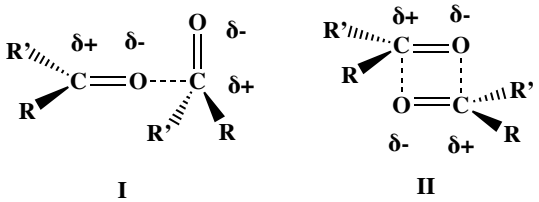
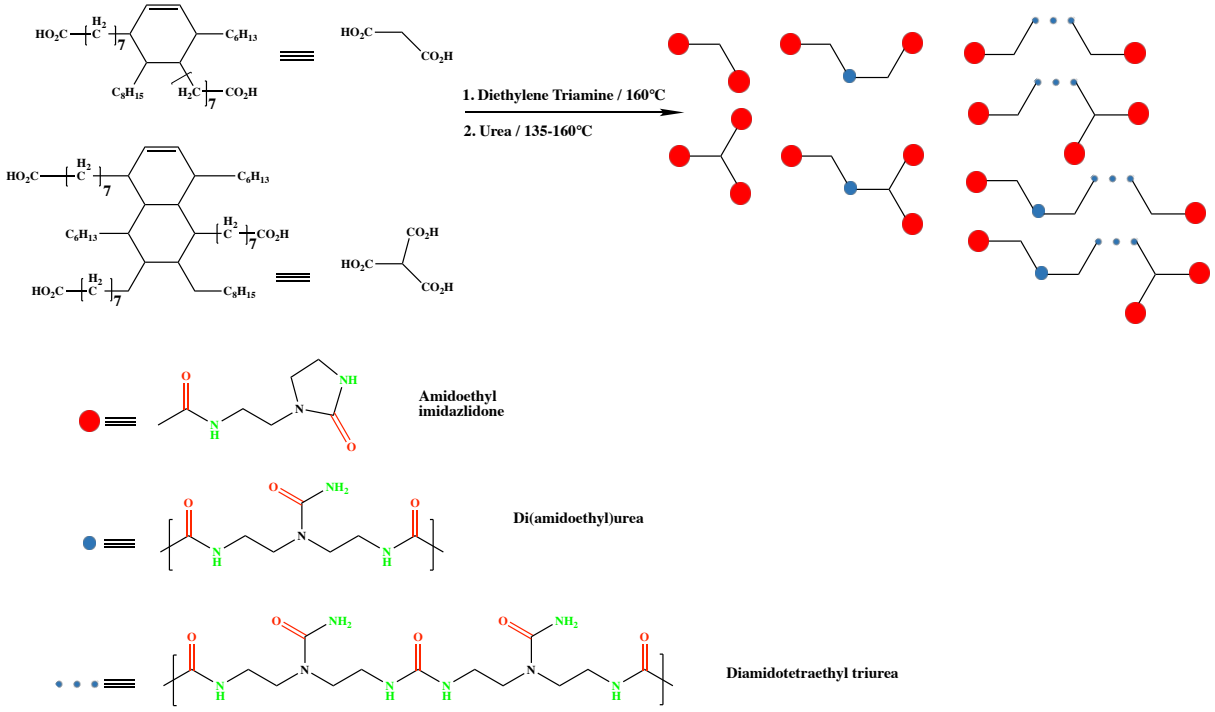


Figure 2. Two types of dipole-dipole in carbonyl compounds.

1.1.4 Hydrogen bonding

Hydrogen bonding is the most common one of weak non-covalent interaction to form supramolecular structures, the general formula is X-H···Y, where X and Y are non-metallic atoms with high electronegativity and relatively small atomic radius like N, O, F etc. X and Y could be either the same or different atoms. Lieber and co-workers reported an example in 2008 (**Scheme 2**), which was an assembly of supramolecular rubber material.[8] Rubber is a common material found in many of items people use every day and is therefore in high demand. The elasticity of rubber, which is an important property of rubber, is easily damaged in some cases, leading to the wasting of resources. This designed rubber framework by Lieber and co-workers via hydrogen bonds between N–H and C=O was found to be a self-healing system which can

be easily repaired by bringing the surface molecules together forming new hydrogen bonds at room temperature when cut or broken. Moreover, the broken-healing process can afford to be repeated for many times without the reduction of the material's extensibility.

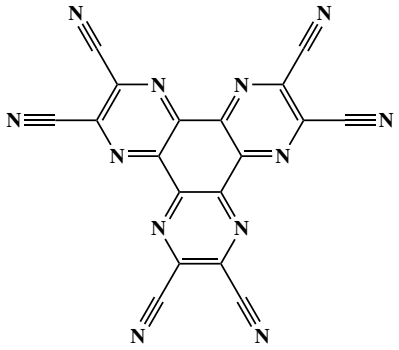


Scheme 2. Lieber and co-workers' hydrogen bond type.[8] Firstly, the mixture of fatty diacid and triacid is condensed with diethylene triamine at 160℃. Secondly, urea is added for reactions, which give a mixture of oligomers with hydrogen bonding groups: amidoethyl imidazolidone, di(amidoethyl) urea and diamidotetraethyl triurea. The hydrogen donors are marked green while acceptors are in red.

1.1.5 Cation- and anion-π interactions

Cation-π interactions are found between alkaline and alkaline earth metals[1] and aromatic or olefinic systems. [9,10,11] For instance, the interaction between K^+ and benzene has an energy of around 80kJ·mol^{-1} compared to that of K^+-OH_2. In 2014, Van Leeuwen and Reek firstly utilized a framework based on Lewis acid and Lewis base interactions. [12] In parallel anion-π interactions have also become topical since around 2002. [13] Anion-π interactions occur between anions and electron deficient arenes. They are increasingly recognised as being common in chemical and biological systems[14,15,16,17], which has become a noted study. For example, Aragay and co-

workers[18] reported a well-known strong electron acceptor $[HAT(CN)_6]^{2-}$ (**Scheme 3**) which forms anion-π interactions with weaker Lewis base anions such as Br^- or I^-.



Scheme 3. The structure of $[HAT(CN)_6]^{2-}$.

1.1.6 π-π stacking interactions

In the building of supramolecular structures, π-π stacking also plays a significant role. The π-π stacking interaction often occurs between aromatic rings which have the opposite electronic properties, one is electron rich while the other is electron deficient. Typically, π-π stacking interaction adopt two types, face-to-face and face-to-edge. (**Figure 3**) In the face-to-face type, the repulsions are serious between the like charges which prevent the formation of face centred examples. However, in the author's undergraduate project which was undertaken in 2016 at the University of Reading, face centred π-π stacking interaction was established between π electron rich species and π electron deficient species. (**Figure 4**) In this example, π orbitals both species are close to each other and get mixed together, which leads to the charge transfer to occur from π electron rich species' HOMO orbitals to π electron deficient species' LUMO orbitals and finally results in the decrease of the energy gap.

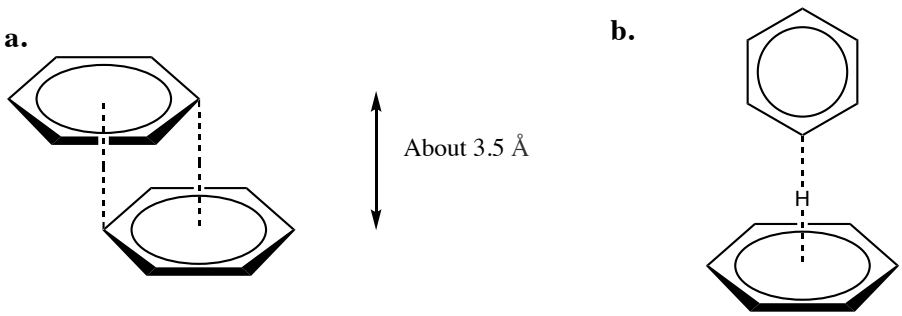


Figure 3. a. Face-to-face π-π stacking. **b.** Face-to-edge π-π stacking.

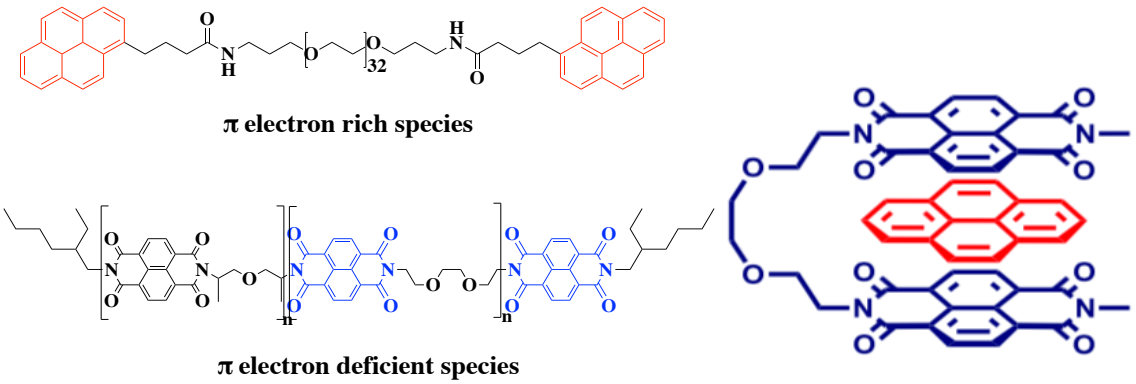
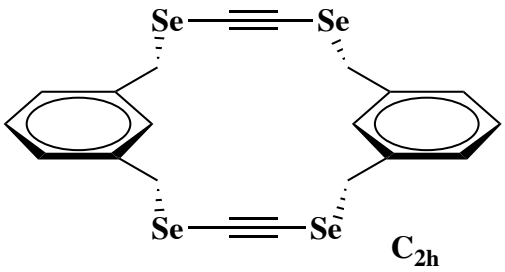


Figure 4. One of the face centred π-π stacking supramolecular structure created by the present author as part of her undergraduate's project.[19]

1.1.7 Van der Waals' forces

Van der Waal's forces represent an interaction that exists between molecules which are nondirectional and weak. It is based on induced dipole-induced interactions, London dispersion forces, and exchange or repulsion forces.[20,22] Van der Waals' forces are caused by the polarisation of an electron cloud when one nucleus approaches the surrounding ones. When Van der Waal's forces are applied in supramolecular chemistry, it plays important roles in 'inclusion' compounds. Lari and co-workers'[21] have reported a supramolecular framework created by metacyclophanes (**Scheme 4**) utilizing CH···π interactions, weak Se···H bonds and intermolecular Se···Se interactions, in which the Se···Se distance is 3.975Å, according to the literature (d=3.91Å), [23] belongs to van der Waals' force. (**Figure 5**)



Scheme 4. The metacyclophane which belongs to space group C_{2h} reported by Lari and colleagues.[21]

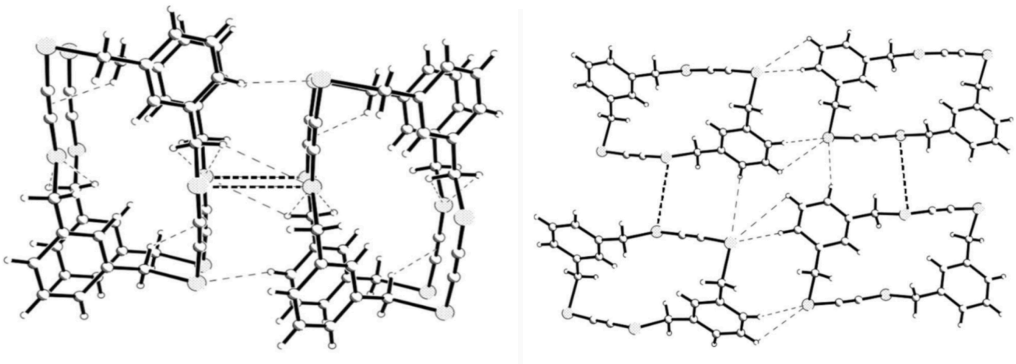


Figure 5. Different interactions in the metacyclophane in **Scheme 4** reported by Lari and co-workers[21] a) CH···π interactions shown by dotted lines, b) light dashed lines are used to indicate the weak Se···H bonds and c) intermolecular Se···Se interactions which belong to Van der Waals force in the supramolecular framework.

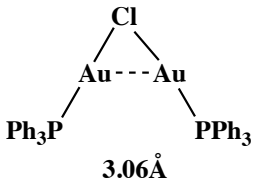
1.1.8 Closed shell interactions

Closed shell interactions are the interactions formed between closed shell atoms whose atomic orbitals have been completely filled with electrons. In general, closed shell atoms of like charges or neutral are not expected to form any meaningful interactions. However, they can give supramolecular structures in some cases, especially for heavy metals with electron configurations between d^8 and $d^{10}s^2$, and heavier halogens. Halogen bonding[24], secondary bonding interactions[25] and metalophilic interactions[26] are included in this kind of interactions.

For instance, halogen bonding involves interactions of type D···X−C. The interaction is formed between the electron-pair donor D and halogen X which is an electron-pair acceptor. The distance between D···X, is a little less than the quantity for Van der Waals' diameter of atoms. In 1863, a model of I_2···NH_3 was published by Guthrie.[27]

Then comes the secondary bonding, which has general X−A···X' type. In which, X usually represents a chalcogenide element or a heavier halogen (Cl, Br and so on). Interestingly, secondary bonding has considerable similarity with hydrogen bonding. The difference is that the H has been replaced by a heavy atom A and often with a high valency (Hg, Tl, Sn, Pb, Sb, Bi, Se or Te). In the formula X−A···X', X−A is classified as a normal covalent bond while A···X' is the truly closed shell interaction and X' donates a lone pair of electrons into the σ* orbital of X−A.

Last but not least, are metalophilic interactions such as the aurophilic interactions between gold atoms, which is called aurophilic interaction. This kind of interaction is prevalent in linear, 2-coordinated Au complexes, commonly in 'A' frame complexes, such as in $[Au_2(\mu\text{-}Cl)(PPh_3)_2](ClO_4)$.[1] **(Scheme 5)**



Scheme 5. Example[1] of $[Au_2(\mu\text{-}Cl)(PPh_3)_2](ClO_4)$ for the aurophilic interaction to show the 'A' frame.

1.2 Gels

Gels have enjoyed popularity for almost a century, and are common features of our daily life. For instance, toothpaste, soap, shampoo and contact lenses are all classified as gels.

Gel has been defined as 'a Nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid' in IUPAC. However, in 1926, Dorothy Jordan Lloyd wrote that "A gel is easier to recognize than to define." Which means that it is clear for the majority of the people what a gel looks like but there are problems when people try to give it a rigorous scientific basis. The first known definition was given by the Scottish chemist Thomas Graham who first gave the rise to the word 'gel', clipping from 'gelatine', in 1861. In his opinion, gelatine appears to hold an important place as a colloidal base, and has similarity with animal fibrin which is a semitransparent, soft, elastic, and stringy solid mass.[28] On account of the gel study on microscopic and macroscopic scale, gels now have a more precise definition.[29, 30] According to the IUPAC definition, gels are colloidal networks which have no liquidity, no flow or a polymer network that runs through its entire volume by fluid expansion.

Gels have been found to have a variety of real-life applications. For example, in the pharmaceutical industry, gels are found useful to control the growth of some drug crystal, not only in terms of growth rate but also the polymorph of the drug. The development of growing crystals in gels started from the tail end of the 18th century and it remained popular until the

1960s. It has recently become topical with the advent of small molecule crystallization in organogels. [31]

Physical gels and chemical gels are well-known distinct classes in the gel world. For a physical gel, especially that made from low molecular weight gelators (LMWG), this kind of gel is produced via physical or non-covalent interactions between gelators and such gels form reversibly, often undergoing a thermally induced sol-gel transition.[32] This property means that the gel can be destroyed and re-formed as many times as tested without the decrease in gelation ability. In comparison, polymer gels are often generated by irreversible chemically cross-linking, to give a permanent network formed by covalent bonds that immobilises the liquid phase. There are two approaches to chemical gelation, additive polymerization and polycondensing the multifunctional units. The gels made in this report are supramolecular gel, a type of physical gel involving non-covalent interactions between small molecules.

1.3 Supramolecular gels

Supramolecular polymers are created based on the formation of non-covalent interactions and self-assembly of the polymer system. The construction of this type of supramolecular system is based on a variety of non-covalent interactions, for instance, hydrogen bonding or metal coordination. The molecules assemble together to establish the network and then immobilize the solvent making gels. Based on the different kinds of solvents, supramolecular gels can be divided into four types, hydrogels[33] which immobilize water, organogels[34] immobilize organic solvents such as methanol, ethanol and so on, aerogels[35] immobilize gas and ionogel[36] immobilize ionic liquids.

Low molecular weight gelators (LMWG) are especially popular in this field. The traditional way to prepare this kind of gels is straightgforward. Warming a solution of gelators and a suitable solvent and allowing it to cool. Gelator concentration is typically 1%-2% w/v or lower.[37] The gelator should completely dissolve to give the sol state. Sonication is a common way usually be used to help break the big gelator particles before heating. In some cases, sonication is applied to the sol-gel process and resulting the formation of sonogels with hybrid organic-inorganic structures.[38] Upon the cooling the mixture, the molecules of gelator undergo supramolecular assembly to create the 3-D nanostructures that mutually interact on the microscale to give an overall sample-spanning network.[39] The network immobilises the

solvents to give stable gels. In other situations which do not form supramolecular structures, the cooling step may give crystals through highly ordered aggregations or microcrystalline or amorphous precipitates from random aggregations.[40]

1.3.1 Supramolecular gels based on metal-ligand bonds

In supramolecular systems, complexes made from organic ligands and transition metal ions play quite important roles. Metal complexes can not only provide the significant architectural components for supramolecular assembly structure, but also give the whole system brand new functions. Besides, various properties of supramolecular polymer can be improved through changing to different metal ions. For the supramolecular gels, metal-complexes based systems have also attracted extensive attention. After the addition of metals, the gel had taken on more new properties like redox activity, photo-electronic and catalytic properties.[41]

1.3.2 Supramolecular gels based on hydrogen bonding

Hydrogen bonding also accounts for a large proportion of supramolecular gels. Indeed hydrogen bonding can be classified as the most common interaction of establishing a 3-D network structure. This report will focus especially on the urea gels[42] and the more unusual squaramide gels[43] which will be discussed separately in the following parts.

1.4 Urea gels

The urea functional group in gelators has been found to be highly effective in gel forming.[42, 44, 45, 46] For urea based gelators, hydrogen bonds form between urea groups (A) to give the urea α-tape motif (B), followed by the formation of the long fibrils (C) via hydrogen bonding, then with the non-covalent interactions fibres or ribbons (D) aggregated and finally the whole self-assembly network (E) established because of entanglement.[42] (**Figure 6**)

According to the literature, bis-urea gelators occupy the majority of the field in urea supramolecular gelators in contrast to mono-ureas. Having another urea group, which means having excess hydrogen bonding interactions shows greater gelation ability. Nevertheless, when the number of urea group increases, tris-urea gelators are surprisingly ineffective in forming supramolecular gels. Adding urea groups in gelators causes a general reduced solubility in non-polar solvents as well as intramolecular hydrogen bonding which might explain the phenomenon.[44]

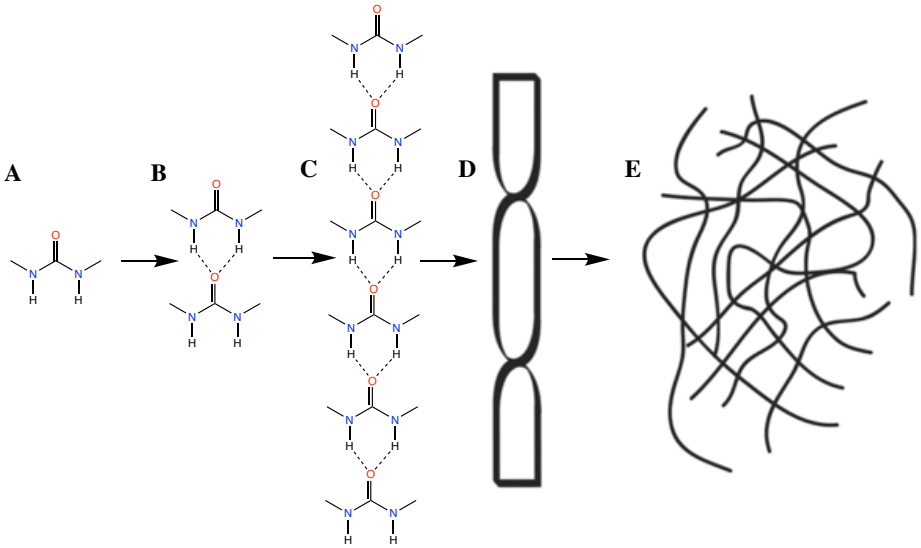


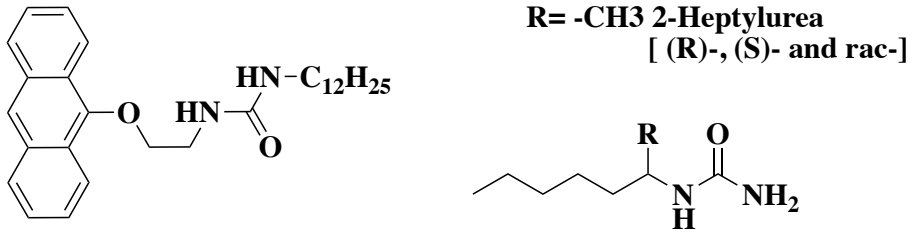
Figure 6. The mechanism to form urea supramolecular gels from A to E.[42]

1.4.1 Mono-urea gelators

Just as its name implies, mono-urea gelators only contain one urea group each and always establishes one-dimensional bonding.[47] For example, the coupling gelator **1.1** (**Scheme 6**) of mono-urea and anthracene formed by Wang and co-workers has been found only gels 1,2-dichloroethane to give an opaque gel at a relatively high concentration (16 mg/mL). The sol-gel conversion occurs at 50℃ and is totally thermally reversible. ^{1}H NMR spectroscopy has been used to establish intermolecular urea hydrogen bonding giving rise to the gel formation, by recording the spectra recorded at variety concentrations of **1.1** to show the aggregation. By changing concentration and temperature the NMR chemical shift is affected, both increasing concentration and decreasing temperature leading the urea resonance to undergo a corresponding downfield shift because of hydrogen bond formation between neighbouring **1.1** molecules and urea groups. At the same time, π-π stacking between anthracene group might also contribute to the formation of the gel alongside the hydrogen interactions.

The next example comes from recent work by Kim *et al.* on heptylurea **1.2** (**Scheme 6**).[48] They compared the gelling ability between *(R)*-, *(S)*- and *rac*-2-hepylyurea. In the gel screen test, both *(R)*- and *(S)*- **1.2** performed quite similarly with the only difference being at the minimum gelator concentration, and showed better gelation ability than the racemic mixture. It was concluded that chiral ureas are apparently more effective gelling agents than racemates. Furthermore, these *(R)*- and *(S)*- mono-ureas rarely formed both hydro- and organo- gels, while racemates gave macroscopic crystals in water. XRD was used to reveal the different

supramolecular structures. Crystallisation for the racemates showed them to have a two-dimensional bilayered structure. *(R)*- and *(S)*- **1.2** alternatively show in a plane and form hydrogen bonding network (**Figure 7**). For the pure enantiomers, 1D fibrous supramolecular framework shaped because the methyl group at the chiral centre has significant steric impact.



1.1 **1.2**

Scheme 6. Examples of mono-urea gelators.

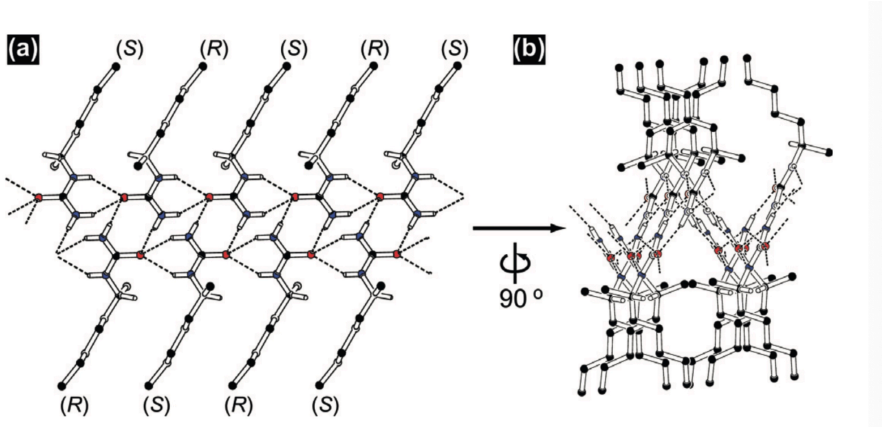


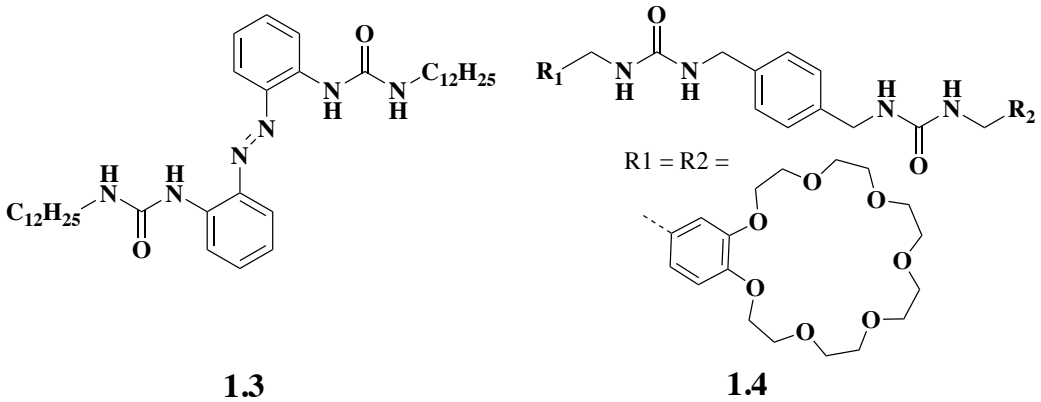
Figure 7. The crystal structure of a single *rac*-2-hepylyurea crystal.

1.4.2 Bis-urea gelators

Bis-urea gelators were first studied extensively in the late 1990s and proved to be highly effective at forming 1D fibres giving rise to gelation of a variety of media.[45] Because in bis-urea gelators, hydrogen bonding takes priority in network assembly, most of the bis-urea gels are thermoreversible.[49]

For instance, the structure shown in **Scheme 7** [50] with an azobenzene spacer in bis-urea gelator **1.3** favours the 1D aggregates creation. Gelator **1.3** displays excellent gelation ability, and gels almost every solvent investigated. The lowest concentration of gelator to form a gel, which is called critical gelation concentration (CGC) for gelator **1.3** is extremely low. Especially in

toluene and *n*-hexane, the CGC even reached as low as 0.2 mg/mL, which is far lower than the minimum concentration (0.3 mg/ML) published as "super-gelators".[51]



1.3 **1.4**

Scheme 7. Examples for bis-urea gelators from Piepenbrock and co-workers[50].

It is worth mentioning that these gels reveal significant thermal stability at higher concentration of gelator **1.3** in *n*-butyl acetate, the melting point exceeds 100℃ (**Figure 8**). According to infrared spectroscopy, two different aggregation types based on polar and non-polar solvents are possible. Both in polar and non-polar solvents, urea groups of gelator **1.3** participated in hydrogen bonding, the only difference is the hydrogen bonding environment in these two kinds of solvents. In polar solvent, each urea group is equivalent while in non-polar solvent each urea group is not equivalent. Additionally, face-to-face π-πstacking between the azobenzene chromopores also contributes to the aggregation, which is displayed through the shift in electron absorption spectrum and builds on Kasha's exciton coupling theory.[52]

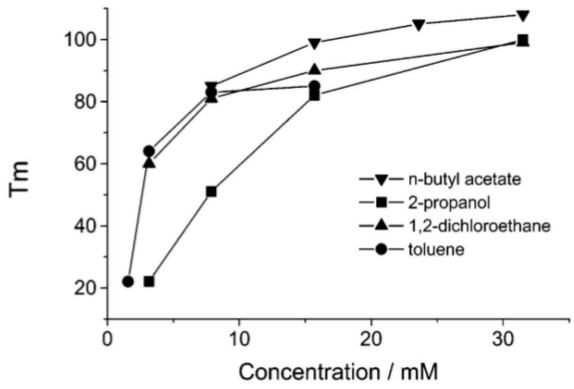


Figure 8. The results of dropping ball experiment to test gel-sol transition temperature for gelator **1.3**.

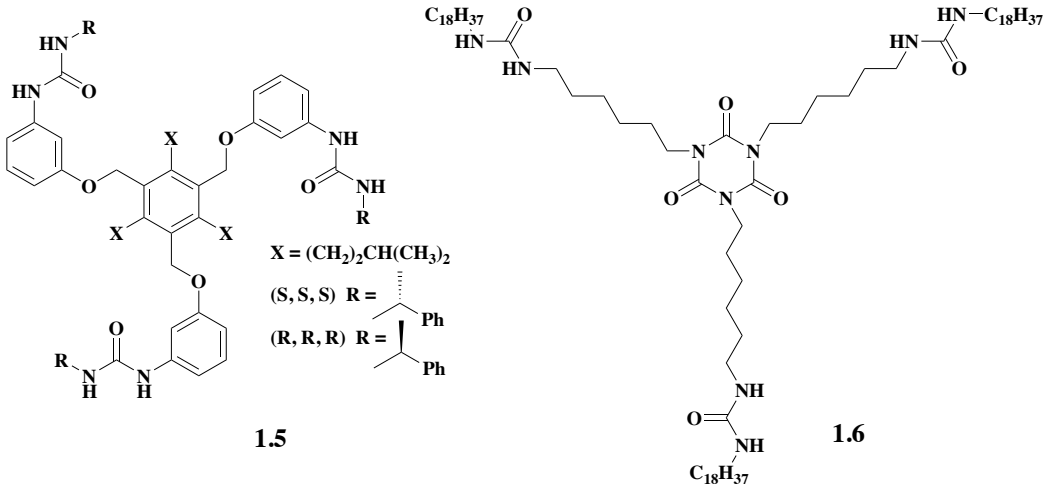
In 2012, Zhenhui and co-workers reported another bis-urea gelator **1.4** (**Scheme 7**).[53] For this gelator, gel formation begins in acetonitrile from 2.2 wt% and yields at partial gel in the other solvents tested, such as methanol, acetone and chlorinated organic solvents. The group used NMR, IR and AFM to study the hierarchical self-assembly structure of gelator **1.4**, particularly whether it is consistent with a former study[54] that suggested it is pivotal for gel formation from linear or cyclic bis(urea) gelators to form an antiparallel arrangement between two urea groups. Firstly, the NH-stretch vibration occurs at 3318 cm^{-1}, which indicates there are hydrogen bonds formed between urea groups in the gel. Then IR spectrum confirmed the existence of bifurcated hydrogen bonds due to the band at 3319 cm^{-1}.[53] Finally, AFM which shows the detail images of gelator **1.4**'s gel state helped to give evidence for the helical aggregation of the gel structure. In the gel formed, not only hydrogen bonding was discovered, but also π-π stacking between the phenyl groups which made contributions to the helical structure, Van der Waals forces between crown ethers which leads to the gel's stability and the superposition of dipole moment on every urea bring an overall increase of dipole moment along the axis. Because the existence of dipole moment, antiparallel arrangement structure enjoys priority for **1.4**, as it confirmed that the dipole moment of two bands could be offset more or less by each other.

1.4.3 Tris-urea gelators

Gelator **1.5** (**Scheme 8**)[55] is a typical example of a tris-urea gelator. Both (*R*, *R*, *R*)-**1.5** and (*S*, *S*, *S*)-**1.5** are able to form gels in 5 different organic solvents, containing toluene, ethyl acetate, methanol, dichloromethane and acetone. However, when (*R*, *R*, *R*)-**1.5** and (*S*, *S*, *S*)-**1.5** are mixed together to get the racemic mixture, there is no gelation. The mixture can still give gels in ethyl acetate, acetone and methanol but with higher CGC than the separate enantiomers. It is worth noting that the enantiomeric excesses of **1.5** affects the CGC, lower enantiomeric excess gives a higher CGC, that is to say the presence of even a small amount of the opposite enantiomer would prominently stop the gelling process. Moreover, as mentioned above, the racemic mixture of **1.5** does not give gel in acetone at the original concentration (2 wt%) whereas a gel is formed in acetone if pre-formed gels of (*R*, *R*, *R*)-**1.5** (2 wt%) and (*S*, *S*, *S*)- **1.5** (2 wt%) mixed at a 1:1 ratio.

What is more surprising is the gel which was produced was quite stable and could bear the mechanical mixing. The phenomenon was explained by the authors as the chiral aggregates were already formed in the pre-prepared gels. However, the randomly arranged racemic which is a mixture of (*R*, *R*, *R*)-**5** and (*S*, *S*, *S*)-**5** had quite poor gelation behaviour. (**Figure 9**)

Another published tris-urea super-gelator **1.6** (**Scheme 8**)[56] shows that poor solubility in common organic solvents at room temperature, whereas it dissolves in several solvents which have high boiling points such as toluene, p-xylene and the aviation turbine fuel, JP-10. Upon heating the solution made from gelator **1.6** and these solvents above 100℃, a clear gel resulted from the solution when it cooled down to room temperature. The gel formed in JP-10 had the lowest CGC of 0.0638wt%, and was selected by the group to carry out further studies on the gel properties. The T_{gel} measurements revealed that the gel in JP-10 has increasing thermostability with increasing concentration of gelator and is thermo-reversible. Moreover, the gel remained in a stable state for a year at room temperature. SEM images of the xerogel show that the non-covalent hydrogen bond formed between urea groups helps create the closely packed 3D network. Then, the most common rheology experiment was conducted to find out the strength of the gel yielded. The thixotropy curves of the gel shows that the viscosity dramatically drops when the shear rate becomes higher, which indicates that the 3D structure breaks with increased shear rate.



Scheme 8. Examples of tris-urea gelators.

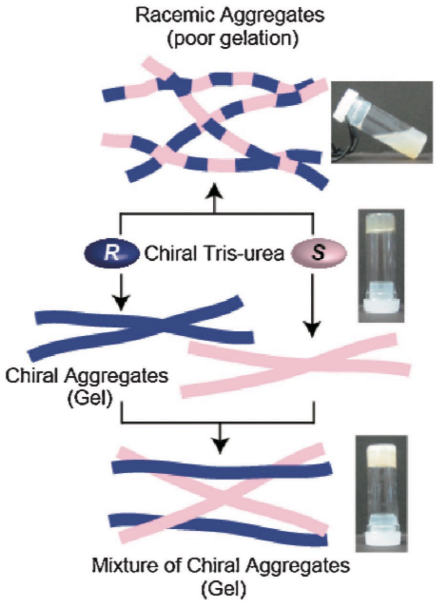


Figure 9. The explanation for the schemes undertaken to form racemic aggregates and chiral aggregates given by Nakagawa and co-workers.[55]

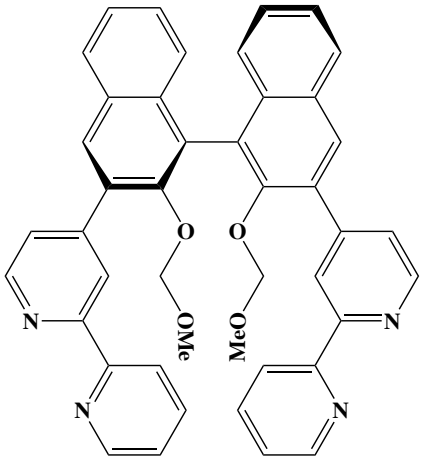
1.5 Metallogels

Metallogelators have become particularly topical in recent years. These gelators which have functional groups that can coordinated with metal centres to form metallogels. The most usual functional group are pyridyl and imidazole[57] groups. Transition metals like Cu, Co, Ni and Ag are popular. Similarly, lanthanide ions are known to give luminescent gels.[58,59]

1.5.1 Silver

Silver has been used by Bian and Gao to produce a metallogel through a chiral bis-bipyridine ligand which has a binaphthyl motif *(S)*-**1.7** (**Scheme 9**),[60] the central silver (I) ion is coordinated to two bipyridyl groups on nearby molecules to form a twisted tetrahedral geometry. In the crystal structure of the supramolecular network established, adjacent sliver centres were bridged by the binaphthyl motify *(S)*-**1.7**. The gelation behaviour could be divided into two steps. The first one is the metal-ligand interaction induced self-assembly, in which a tubular helical homochiral coordination polymer formed. This process is followed by the creation of a the 2-D multi-layered structure and then laminar-structured nanofibers by utilized π-π interactions.

The same group then extended this work[61] on **1.7** but using the racemate. This racemic analogue showed significant differences in gelation properties compared to Ag(I) complexes of the chiral ligand. It took a longer time and needed a higher concentration to form the gel, and the temperature of sol-to-gel transition was discovered to be very much lower than the chiral case. At the same time, the gel was not stable and crystallised to single crystals at room temperature after 6 hours. The crystal structure shows a square-pyramidal geometry with metal-ligand interactions between central silver and the approximately coplanar two bipyridyl units.



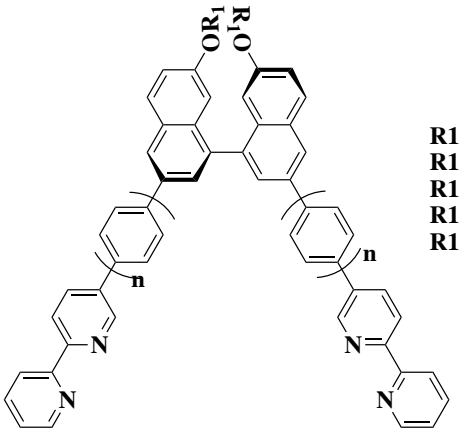
(S)-1.7

Scheme 9. Structure of the ligand designed by Bian and Gao which contributes to form metallogel with Ag(I).[60]

1.5.2 Copper

Copper is quite a common metal used in the formation of metallogels. For example, a multi-responsive class of Cu(I) metallogel **1.8-1.12** was reported in 2010, by Gao and co-workers[62] (**Scheme 10**). Upon adding $Cu(CH_3CN)_4BF_4$ into the mixture of **1.8-1.12** and organic solvents, with a sonication step, a dark green metallogel formed as a result of 1-D polymerisation. The Cu(I) centre helps to create a highly ordered network (**Figure 10**). As the gel system is multi-responsive, it could form a sol state upon the addition of pyridine, heating it up and oxidizing the central Cu(I) to Cu(II). For applications, the Cu(I) metallogel performed well as a catalyst for the Huisgen 1,3-dipolar cycloaddition, which is called the "click" reaction. During this experiment, **1.10** was found to be the most outstanding catalyst at room temperature in the water-air environment because of its long lipophilic carbon chain, which provides an organic microenvironment for the reaction in the water medium. Furthermore, the catalytic ability of the catalyst was not lost when reused.

Copper(II) metallogels have also been reported with 1,4-dodecyloxy-bis(4-benzoyl-L-glutamic acid) **1.13** and bolaamphiphilic *N,N'*- hexadecanedioyl-di-L-glutamic acid **1.14**, (**Scheme 11**) reported by Liu and co-workers.[63,64] They first found that a hydrogel was formed with **1.13** and **1.14**, then Cu(II) was introduced to the system as Cu(II) could assist in stabilising the nano-framework and play a role as a catalytic centre in organic reactions.[64,65] However, only **1.14** gave a gel in the presence of Cu(II). Comparing the SEM of pure **1.14** and Cu(II)-coordinated **1.14**, a thinner tubular morphology was noted compared to the monolayer helical nanotubes of pure **1.14**. XRD was also carried on for both pure **1.14** and Cu(II)-coordinated **1.14**. Only one diffraction peak showed in the XRD of the pure **1.14** hydrogel which revealed the layer distance in the self-assembled structure and when Cu(II) was added, the original peak got stronger as well as having two new peaks appear that showed the transformation from a structure with a single layer to the multi-layered nanotube. By comparison, structure **1.13** only gave gels by itself, while Cu(II) resulted in precipitates in belt-shaped morphologies according to the electron microscopy images. This change was attributed to the rigid structure of the aromatic ring stopping the self-assembled framework becoming more stable upon metal-ligand interaction. In terms of catalytic ability, Cu(II)-coordinated **1.14** proved more effective than pure **1.13**, with a faster reaction rate and higher enantioselectivity in the Diels-Alder reaction between cyclopentadiene and aza-chalcone. The probable explanation could be that copper ion on the surface of the multi-layered nanotube offered a favoured environment for the DA reaction in respect of stereochemistry.



R1 = CH_2OCH_3; n= 1 1.8
R1 = CH_2CH_3; n= 1 1.9
R1 = n-C_6H_{13}; n= 1 1.10
R1 = n-C_6H_{13}; n= 2 1.11
R1 = CH_2CH_3; n= 0 1.12

Scheme 10. Examples of copper (I) metallogel **1.8-1.12** reported by Gao.

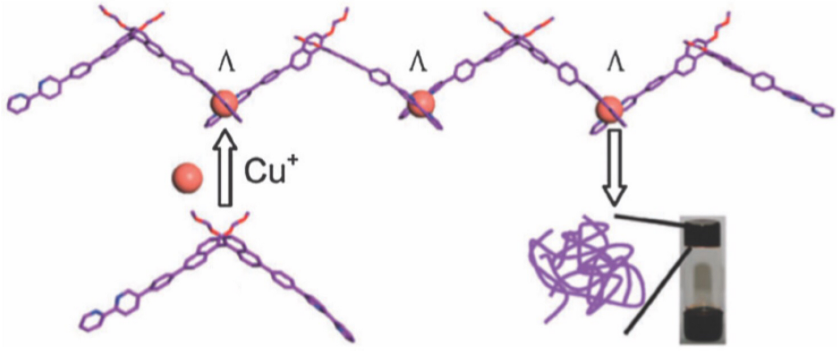
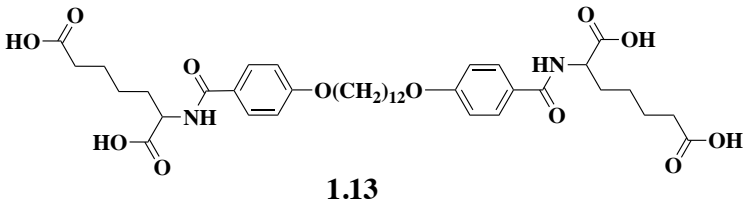
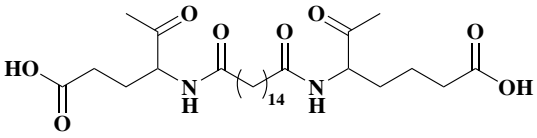


Figure 10. The supramolecular network shaped upon the metal-ligand interaction between copper (I) and **1.8** which immobilize the solvent.



1.13

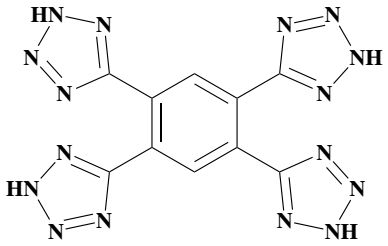


1.14

Scheme 11. The structure of **1.13** and **1.14** reported by Liu and co-workers.

1.5.3 Cobalt

Co(II) is another widely applied central metal ion to establish a supramolecular network based on metal-ligand bonds. An example reported by Shinkai and co-workers[66] has the applications as a selective chemsensor which has selectivity and could detect chloride utilising the conversion of the metallogel. Compound **1.15** was found to give gels in polar solvents in the presence of Co(II). It is interesting that only the addition of $CoCl_2$ led to blue metallogels because of the formation of tetrahedral Co(II) complexes comparing with other cobalt salts, which formed red metallogels having octahedral Co(II). When HCl gas is passed through the gel, drastic colour changes from red to blue took place, revealing the framework transforms from octahedral to tetrahedral. Meanwhile, when the non-chloride cobalt-coordinated metallogels were exposed to other halogen gases, such as HI, HBr and HF, no colour changes were observed during the experiment. Even low concentrations of HCl gases loaded within a capillary whose inner diameter is only 50μm could be detected using this method.



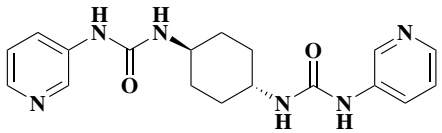
1.15

Scheme 12. The structure of **1.15** reported by Shinkai and co-workers to form metallogel with Co(II).

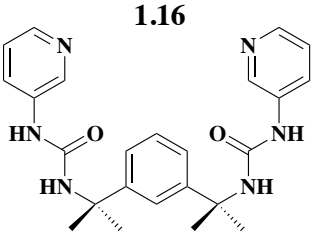
1.5.4 Bis-urea metallogel

In the research of metal-ligand interaction based supramolecular urea gels, Cu(I) and Cu(II) are frequently chosen to play the central metal roles. Steed and co-workers have studied ureas which are not gelators themselves but could form metallogels after the addition of copper (II).[67,68] (**Scheme 13**).

Compound **1.16**, gave a crystalline gel after the addition of Cu(II) nitrate and the structure of the metallogel was shown by TEM image to comprise well-defined ribbons with a wide range of widths. The same group subsequently carried out a systematic study on how the Cu(II) concentration would affect the stability of the metallogel made from **1.17**. As **1.17** itself is not a gelator in organic solvents but a metallogel which is obtained after the addition of $CuCl_2$ due to the building of the metal-ligand interaction between Cu(II) and the terminal pyridyl groups. When the concentration of Cu(II) increased, the whole system undertook the transformation from sol to gel then further to crystals. Between the 0.1 and 0.5 equivalent of $CuCl_2$, the gel changed from a blue partial gel to a strong gel with T_{gel} increasing. When the concentration of $CuCl_2$ increased beyond a 0.5:1 ratio, the gel system was disrupted and green $[Cu_3(\mathbf{1.17})_4Cl_4]Cl_2 \cdot nH_2O$ (n=ca. 16) crystals grew. The material was characterised by PXRD. The PXRD pattern of the mixture as the $CuCl_2$ concentration was increased to 0.5 equivalent and then higher, changed from signals which are highly resolved to broad and featureless signals and finally to a much sharper diffraction pattern. This revealed the structural transformation from well-ordered to amorphous and finally crystalline material. Also $Cu(NO_3)_2$ was examined to determine whether a gel would form but this system only gave crystals, which indicated that the gel formation was dependent on the nature of anions.



1.16



1.17

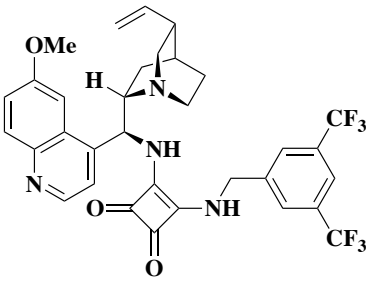
Scheme 13. The urea moieties tested by Steed and co-workers to form the metallogel with Cu(II). [67,68]

1.6 Squaramides

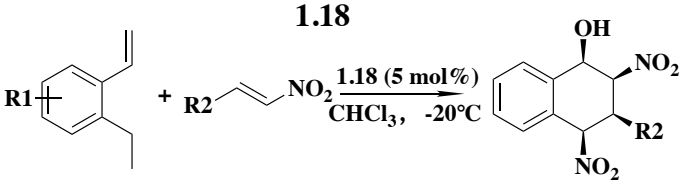
1.6.1 General properties of squaramides

Squaramide was first prepared in 1966 and synthesized by Maahs and Hegenbergs from vinylogous amide.[69] In recent research, squaramide and its derivatives have been applied in various fields including organocatalysis, organometallic chemistry, medical chemistry, material science, ion recognition and bioconjugate chemistry.[70]

In organocatalysts, chiral squaramides are well studied. It is believed that these squaramides are alternatives to the guanidine and urea/thiourea catalysts. Enders and co-workers reported their use in domino/cascade reactions.[71] The squaramide **1.18** was added into the domino Michael/Henry reaction (**Scheme 14**) and provided high yields and high diastereomeric ratios, as well as showing high enantioselectivities.



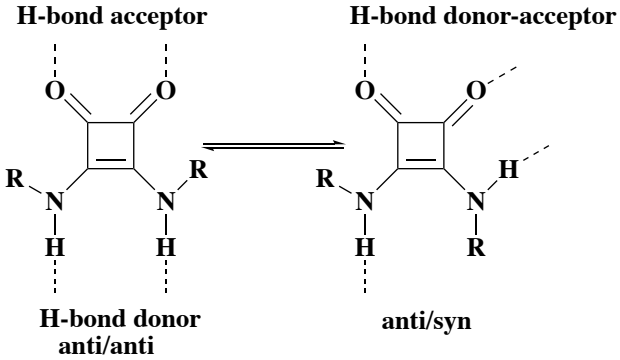
1.18



Scheme 14. The structure of squaramide **1.18** and the reaction it catalysed.

1.6.2 Squaramides in supramolecular chemistry

The squaramide group has a quite rigid four-member-ring structure which contains a 2-π electron, it also has aromaticity, which is quite strong compared with the benzene ring.[71] Moreover, squaramides have been mentioned often together with ureas due to their similar characteristics in hydrogen bonding. Costa, Diya and co-workers have pointed out that hydrogen bonding of the secondary squaramides could allow them to act as acceptors, donors or acceptor-donor groups.[72] (**Scheme 15**)

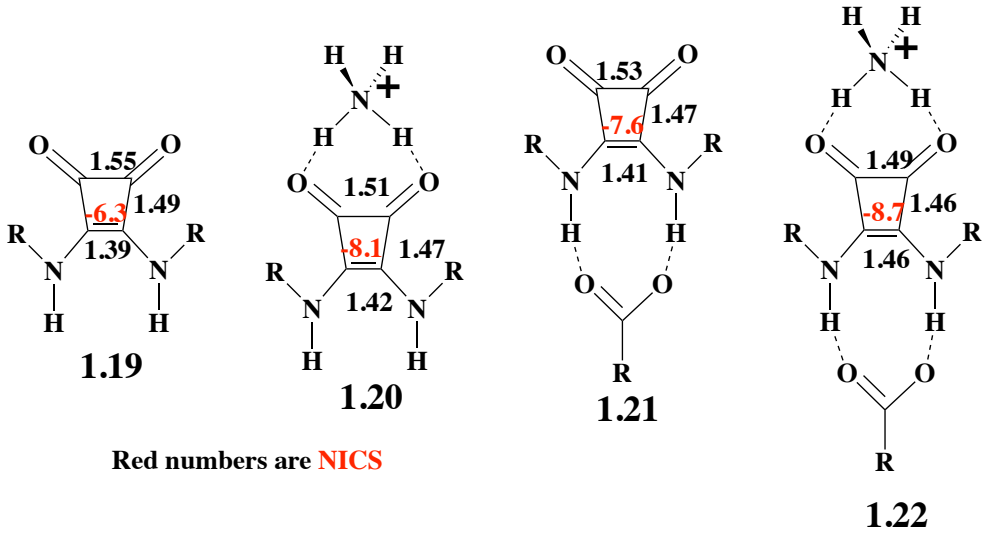


Scheme 15. The donor-acceptor potential of hydrogen bonding of squaramides.

The hydrogen bonding-acceptor character of squaramides make them outstanding in the field of ammonium ion recognition.[72,73] Deya *et al.* carried out a calculation for squaramide **1.19** and its complex with ammonium cations **1.20** to determine their potential as hydrogen bond acceptors (**Scheme 16**)[74]. The group measured aromatic stabilisation energies, bond length and nucleus independent chemical shifts (NICS) in order to compare the aromaticity, structural difference and magnetic properties. The final results showed that squaramide **1.19** functioned as a good hydrogen bond acceptor. The probable reason is the NICS (0.6) data changed from -6.3 ppm to – 8.1 ppm with the addition of ammonium cation which revealed the increase of aromaticity on the squaramides.

Squaramides can also act as the hydrogen bond donors. Deya and co-workers discussed the hydrogen bonding of squaramides to carboxylate anions.[75] The binding of anions and squaramide was quite successful, and the complex persisted even in water, where the hydrogen bonding despite strong solvent competition. The NICS (0.6) was also evaluated and found to show increased aromaticity. (**Scheme 16**)

A model of squaramides with both ammonium cations and carboxylate anions was established and **1.22** became the most aromatic one of the four **1.19**, **1.20**, **1.21** and **1.22** which indicated the possibility to form all the predicted hydrogen bond patterns, highlighting the importance of aromaticity augments in the system. (**Scheme 16**)



Scheme 16. The actual structure of squaramide **1.19**, hydrogen bond acceptor squaramide **1.20** with ammonium cations, hydrogen bond donor squaramide **1.21** with carboxylate anions and modelled donor-acceptor squaramide **1.22** with both ammonium cations and carboxylate anions. (All bonds' length of squaramides have been labelled.)

1.6.3 Squaramide gels

As squaramides have been found to be effective hydrogen bond receptors, the applications of squaramide and its derivates in gel chemistry is a logical step, although they have not been extensively studied.

Díza and co-workers reported the squaramide-based gelator **1.23**[76] (**Scheme 17**). A total of 34 solvents were tested for the gelation ability with this compound over a large range of concentrations. The gelator was found to be insoluble in 9 solvents even when sonication was used. However, it is interesting that gelator **1.23** displayed great gelation capability in alcoholic solvents containing branched, linear, primary, secondary and tertiary alcohols such as methanol, ethanol, phenylmethanol and so on. The CGC have been examined for the gels obtained and had a range from 3 to 21 g L^{-1}. Moreover, some of the gels obtained were not only thermoreversible, but also enjoyed an increase in gel stability and gelation kinetics after the destruction and reformation processes, which indicated a more robust framework formed

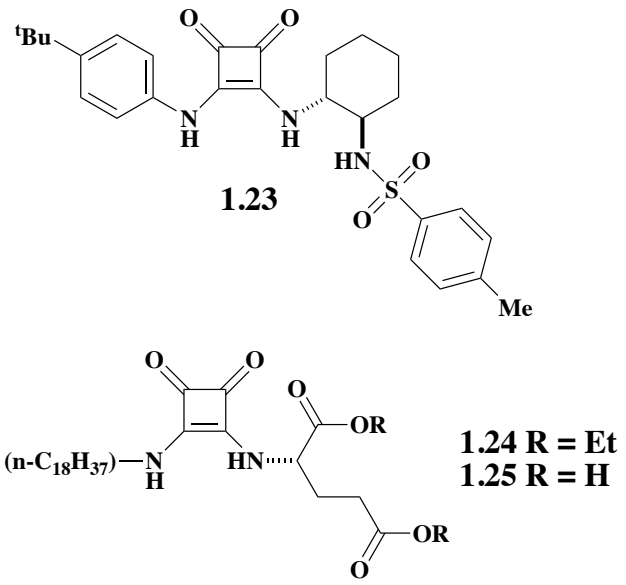
because the thermodynamically more stable aggregates were protected from gel-to-sol transition. Rheology however indicated that the gels formed were quite weak.

UV-vis measurements, FTIR and NMR were used to confirm the interactions involved in the supramolecular network. Comparing the FTIR spectrum of both xerogel and **1.23** in solution, tiny variations in frequency moving to the lower wave number occurred which suggests the existence of both hydrogen bonding and π-π stacking interaction. The suggestion was supported by UV-vis results during the sol-to-gel transformation and NMR measurements.

Díza and co-workers also reported squaramide-based gelators **1.24** and **1.25** two years later[77] (**Scheme 17**), which were screened for gel formation in 22 solvents ranging from polar protic, polar aprotic and apolar using the traditional heating-cooling cycle to prepare samples.

The gelator **1.24** dissolved into 8 different solvents including water, while 12 of 22 solvents resulted in gel formation and in most of cases, gelation took place in under 30 minutes. Within the 12 gelled solvents, CGC values possessed a huge range, from 16 ± 1 to 180 ± 20 (g/L). All gels were found to be opaque and white in colour which revealed the size of the supramolecular network exceeds the wavelength of visible light (380-780nm), and evidence from electron microscopy supported this argument. Furthermore, all the gels proved to be completely thermoreversible and could maintain the gel states for at least 2 months, with only the one in DMF crystallising.

In contrast, the gelation ability of gelator **1.25** was surprisingly low when compared to similar structures replacing the squaramide with N-stearoyl-L-glutamic acid or 1,4-disubstituted 1,2,3-triazole as both of these structures proved to be good gelators. Four different gels were found in chloroform, methanol, propan-2-ol and toluene for **1.25**, while **1.24** did not gel the chloroform and toluene.



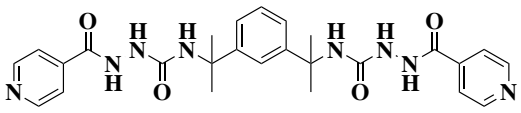
Scheme 17. The squaramide-based gelators **23**, **24** and **25** put forward by Díza and co-workers.

2 Project Aims

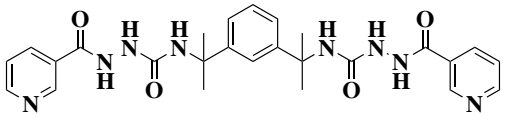
Novel small molecule gels are increasingly being used as crystallization media for producing new forms of pharmaceuticals. These novel crystal forms may have altered dissolution characteristics and bioavailability and hence are of significant potential importance in the pharmaceutical industry. The overall aim of this project is to establish a supramolecular framework based on hydrogen bonding and metal-ligand interactions in order to form gel systems, and test the gelation abilities of these new compounds. A key aim is the comparison of the strength of which squaramides and bis-ureas gels.

Squaramides in particular offer the possibility of acting as extremely efficient hydrogen bonding receptors and hence may create a particular robust supramolecular gel network. Squaramides were prepared by Dr Rob Elmes at Maynooth University, Ireland and one aspect of this work in collaboration with Maynooth involved testing their gelation properties as well as the materials characteristics of the resulting gels and comparing them to their urea-based analogues.

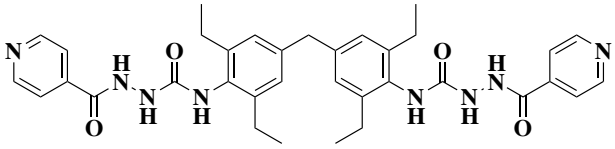
As part of this project, urea-based compounds **2.9** – **2.12** (**Scheme 18**) have been synthesized firstly for metallogel-screening, especially for **2.9** which bears isoniazid pendant groups and **2.11** terminated with nicotinic hydrazide. Secondly, because **2.9** and **2.10** have been previously reported, [77] it is interesting to see if their analogues could be found to contain similar gelation abilities.



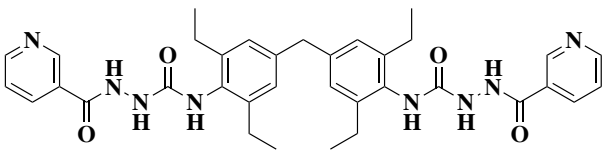
2.9



2.11



2.10



2.12

Scheme 18. The chemical structure of **2.9**-**2.12**.

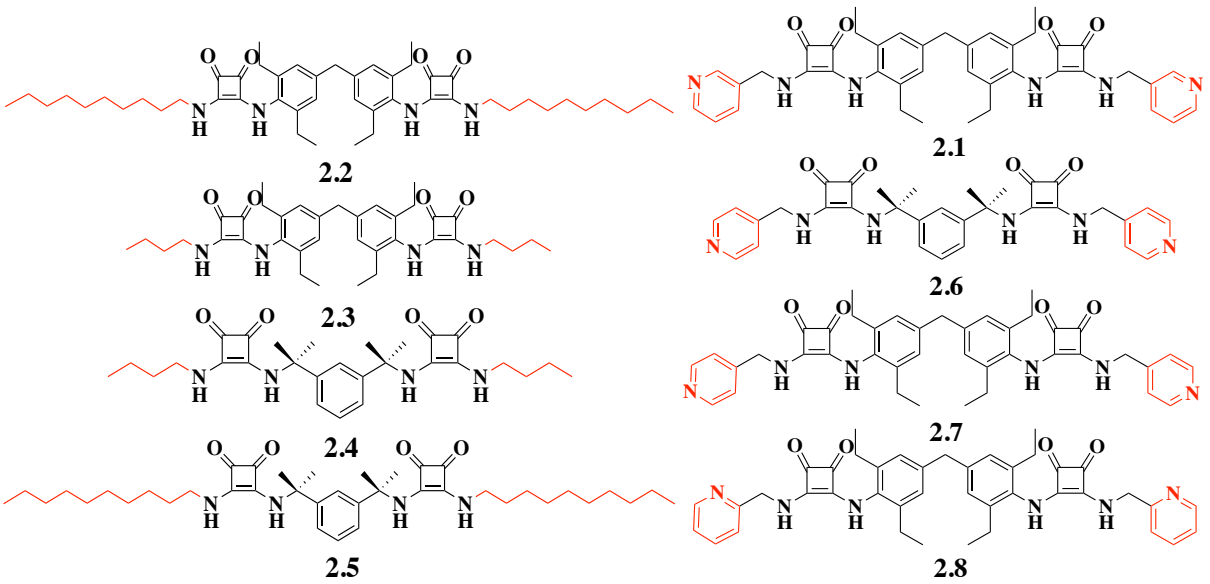
Finally, all urea and squaramide gels will be characterised by rheology and SEM in order to compare and contrast their materials properties and provide insight into their network structures.

3 Results and discussion

3.1 Synthesis of gelators

3.1.1 Squaramides

Squaramide-based compounds **2.1 - 2.8** were synthesized and characterized by Dr Rob Elmes at Maynooth University, Ireland. The eight squaramides can be divided into two different categories because of the ending groups (ending with pyridinylmethyl or alkyl groups). (**Scheme 18**)



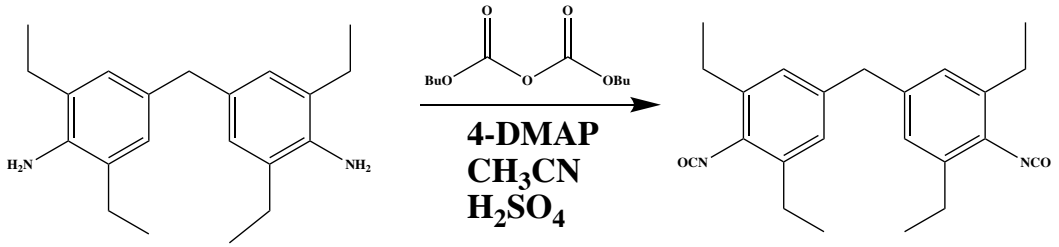
Scheme 18. The structures of the 8 squaramides in two different classes involving either alkyl or pyridinylmethyl terminal groups.

3.1.2 Tetraethyl diphenylmethane diisocyanate linker

The tetraethyl diphenylmethane diisocyanate linker is a common linker used extensively by the Steed group and often proves to give rise to highly effective gelators in conjuction with ureas. The parent diisocyanate was synthesized from the reaction between 4,4'- methylenebis(2,6-diethylaniline) and di-tert-butyl dicarbonate with a yield of 89% as a white solid state (**Scheme 19**).[78] The reaction is air and water sensitive so is carried out under an N_2 atmosphere and dry acetonitrile is used as the solvent.

The structure of the tetraethyl diphenylmethane diisocyanate linker was characterised by NMR spectroscopy. Comparing the ^{1}H NMR spectra of the starting material 4,4'-methylenebis(2,6-diethylaniline) and diisocynate linker, the resonance of the -NH_2 group disappeared at around

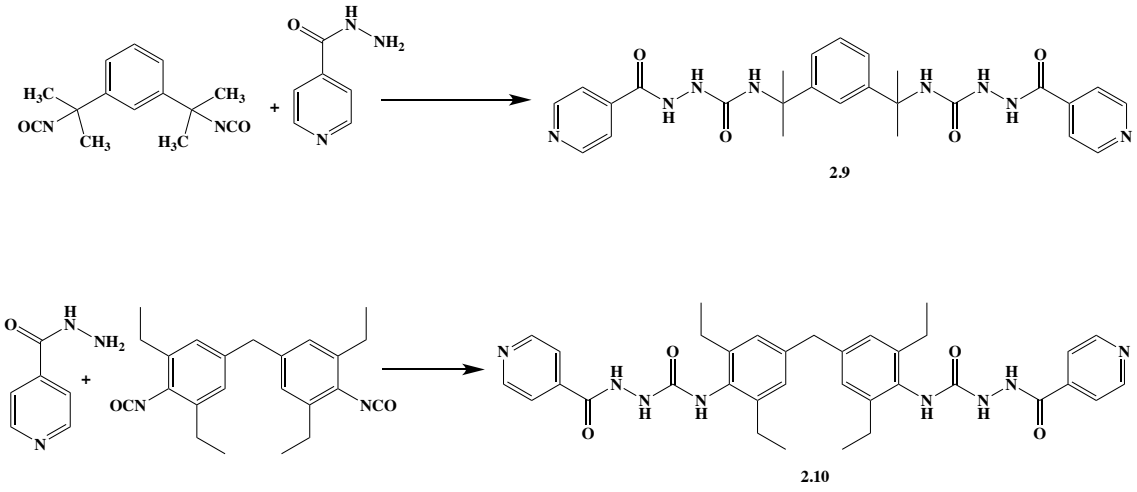
3.50ppm and all signals moved towards low field which indicated the transformation from -NH_2 to -NCO.



Scheme 19. The synthesis of the precursor diisocynate used to prepare tetraethyl diphenylmethane diisocyanate based bisureas.

3.1.3 Isoniazid derived gelators 2.9 and 2.10

Compounds **2.9** and **2.10** have been previously reported by Steed and co-workers.[79] Isoniazid was added to the relevant linkers (meta-disubstituted aryl linker for **2.9** or tetraethyl diphenylmethane diisocyanate linker for **2.10**) in chloroform and ethanol, followed by the catalyst triethylamine. The mixture was refluxed for 24 hours and the products filtered out to give the white solids in excellent yields 92% for **2.9** and 89% for **2.10**. NMR and mass spectroscopy were employed to characterise the materials and the data matched the previous work well.[79] Compound **2.9** was further characterised by single crystal X-ray crystallography, and will be discussed later in section **3.2.3**.



Scheme 20. Synthesis schemes of **2.9** and **2.10**.

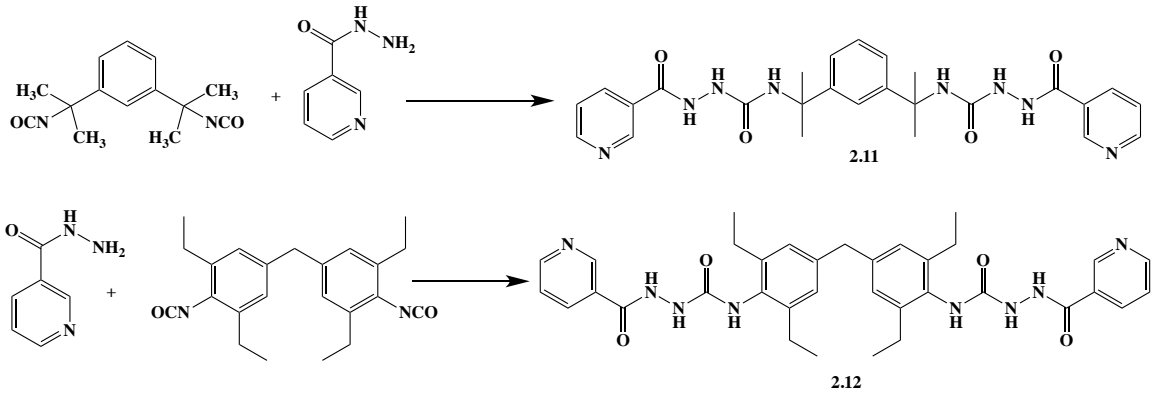
In the ^{1}H NMR spectrum of **2.9** and **2.10**, the chemical shift of the isoniazid derived NH group increases due to the newly formed bond between C=O and -NH which is caused by the reduced

electron density. At the same time, the ^{13}C NMR spectrum is consistent with the expected number of aromatic carbon atoms in the structures. Moreover, accurate mass spectroscopy confirmed the protonated structures and was consistent with the calculated molecular weight with an only 1.6 mDa and 0.9 mDa difference, respectively.

3.1.4 Nicotinic hydrazide derived gelators 2.11 and 2.12

Compounds **2.11** and **2.12** are analogues of **2.9** and **2.10** with a para-substituted pyridyl ring as opposed to the meta isoniazid derived geometry. These compounds were prepared in the same way as **2.9** and **2.10** were prepared in good yields of **2.11** (87%) and **2.12** (87 %)

In the same way as **2.9** and **2.10**, compounds **2.11** and **2.12** were also could be characterised by ^{1}H NMR spectroscopy. For **2.11**, three NH peaks in different chemical environments were displayed at ca. 10.34, 9.00, 8.71 ppm and all the peaks for the aromatic ring CH protons could be assigned. For **2.12**, the peaks for NH protons occurred at 10.44, 9.04, 8.69 ppm. The ^{13}C NMR spectra also agree well with the predicted structures. Accurate mass spectroscopy acted as further confirmation of the structures, both **2.11**and **2.12** displayed molecular ion peaks for the protonated compounds with a difference between the calculated and experimental mass of 0.2 and 1.7 mDa, respectively.

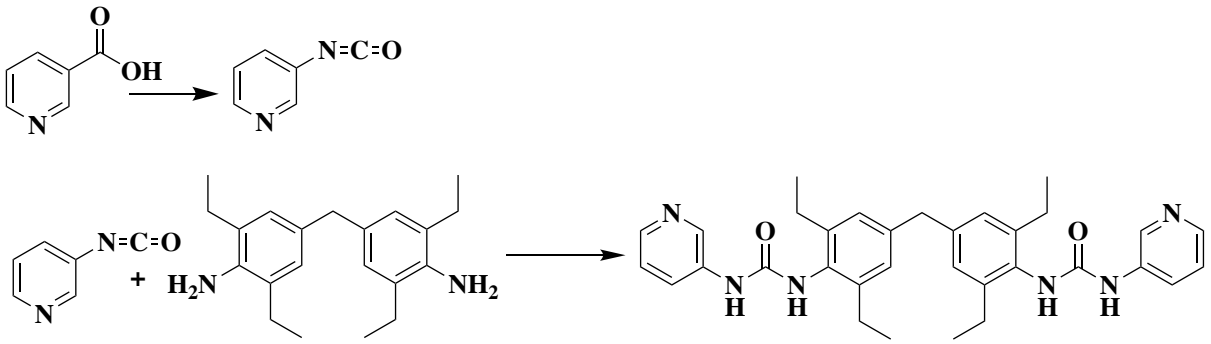


Scheme 21. Synthesis of **2.11** and **2.12**.

3.1.5 Gelator 2.13

The synthesis of **2.13**[67] requires the preparation of 3-pyridyl isocyanate from the nicotinic acid first. After preparing the isocyanate, directly into the mixture, the diamine 4,4'-methylenebis (2,6-diethylaniline) is subsequently added. Finally, a white solid was achieved in a yield of 86% after filtration and drying.

According to the ^{1}H NMR spectrum, the integration of the NH peak at 8.96 ppm appears low as a result of its broadness of NH while all other integrations were consistent with the proposed structure and matched those reported previously.[67] In addition, the ^{13}C NMR spectrum was also consistent with the literature.



Scheme 22. Synthesis of compound **2.13**.

3.1.6 Some comments on the Elemental analysis results of 2.9-2.12

Elemental analysis is commonly used to characterize organic compounds by showing the elemental composition with a normally error less than 0.5%. In this thesis, elemental analysis was carried out on new compounds **2.9-2.12**. However, despite HRMS data matching the calculated formula, analytical data indicated the presence of significant impurities (see experimental section) For compound **2.11**, the discrepancy on the percent carbon was around 1% which might arise from the presence of the residual chloroform used both as the reaction and washing solvent. For compounds **2.9**, **2.10** and **2.12,** quite large errors have been found at elemental analysis, with observed percent carbon being particularly low. Since the ^{1}H and ^{13}C NMR spectra do not indicate the presence of organic impurities, it is likely that the sample is contaminated by residual inorganic impurities or compound low in carbon, particularly chloroform. For example, according to the ^{1}H spectrum of **2.9** (**Figure 11**), there are no significant signals not arising from the target compound except for the solvent peaks, including chloroform. The same situation was also found for **2.10** and **2.12**. The only point worth mentioning on the ^{1}H NMR spectra for the analogues **2.10** and **2.12** is the peak for the CH_2 on the ethyl substituents masked by the DMSO solvent peak, but DMSO is the only solvent in which compounds **2.10** and **2.12** dissolve. In some cases, some mass loss during the elemental analysis process was noted and hence more rigorous drying could be attempted if the project had more time. Traces of residual chloroform or inorganic impurities are not expected to have

a significant effect on the gelation results and recalculating the analysis data to account for residual chloroform yields reasonable results (see experimental section).

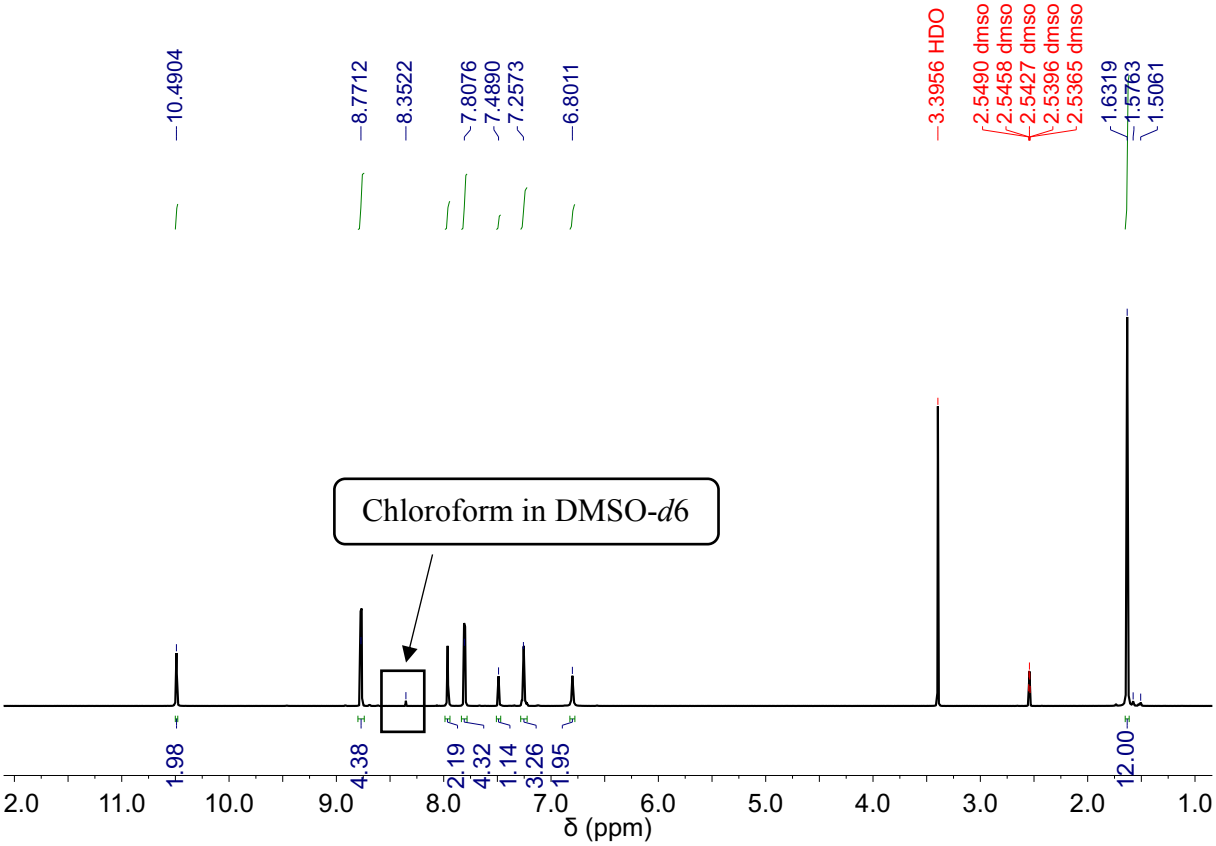


Figure 11. ^{1}H and ^{13}C NMR spectra of compound **2.9**.

3.2 Gel screen results

3.2.1 Gel screen results for pyridinylmethyl terminated squaramides

All of the pyridinylmethyl terminated squaramides were tested both by themselves and along with solutions of several metal salts in15 solvents: 1,2,4-TCB, 1,2-DBE, 2-Butanone, 1,2-DCB, 1,4-dioxane, 2-picoline, ACO, ACN, benzyl alcohol, chloroform, cyclohexane, diethylene glycol, ethanol, toluene and water. The concentration of gelators was 1%w/v and metal solution were added at 0.5 equivalence relative to the gelator.

Compounds **2.1**, **2.7** and **2.8** performed to be similarly poor in the gel screen test. All these three squaramides could not completely go into the tested solvents after being sonicated and heated, which finally led to no formation of gels. Afterwards, 1%w/v $CuCl_2$ in methanol solution (0.5eq) has been added, however, this attempt to bring out further cross-linking was unsuccessful as there still did not form any gel.

In contrast, compound **2.6,** which is the only pyridyl containing squaramide gelator without the diphenylmethane derived spacer, revealed quite different results. While it was not a gelator by itself, it formed effective metallogels in presence of $CuCl_2$ in methanol solution **(Table 1)**. The most effective gels were formed from 1,2,4-Trichlorobenzene and 1,2-DCB, which gave homogeneous gels. (**Figure 12**)

Table 1. Gel screen results of compound **2.6** at 1%w/v with the presence of 0.5 equivalence metal ligand solutions.

2.6	**1% w/v**	**$CuCl_2$**	**$Cu(NO_3)_2$**	**$Co(NO_3)_2$**	**$Ni(NO_3)_2$**
1,2,4-TCB	ppt	G	ppt	ppt	ppt
1,2-DBE	ppt	ppt	ppt	ppt	ppt
2-Butanone	ppt	ppt	ppt	ppt	ppt
1,2-DCB	ppt	G	ppt	ppt	ppt
1,4-Dioxane	ppt	ppt	ppt	ppt	ppt
2-Picoline	ppt	ppt	ppt	ppt	ppt
ACO	ppt	PG	ppt	ppt	ppt
ACN	ppt	PG	ppt	ppt	ppt
Benzyl Alcohol	ppt	PG	ppt	ppt	ppt
Chloroform	ppt	ppt	ppt	ppt	ppt
Cyclohexane	ppt	ppt	ppt	ppt	ppt
DEG	ppt	ppt	ppt	ppt	ppt
Ethanol	ppt	PG	ppt	ppt	ppt
Toluene	ppt	PG	ppt	ppt	ppt
Water	ppt	PG	ppt	ppt	ppt

ppt-precipitate, PG-partial gel, G-gel.

A.  **B.**  **C.** 

Figure 12. Gels of compound **2.6** found **A.** in 1,2,4-Trichlorobenzene, **B.** in 1,2-DCB and C. in Methanol. All concentrations are the same 1% w/v with the presence of 0.5 equivalents of $CuCl_2$ methanol solution.

3.2.2 Gel screen results for alkyl groups terminated squaramide gelators

Gelation tests for the alkyl groups terminated squaramides were carried on the same 15 solvents as well as the pyridinylmethyl analogues. Based on the outcome of the rheology tests, **2.2** gave quite weak but clear gels in about one-third of the solvents tested at 1% w/v. (**Figure 13**) However, compared with gelator **2.2**, squaramides with the same diphenylmethane derived linker but different lengths of the alkyl groups, gelator **2.3** had really poor gelling behaviour and only one sol-like partial gel was found in 1,4-dioxane. The possible reason might be the longer alkyl chains entangle to help form the supramolecular network as well as increasing the hydrophobicity of the compound.

Interestingly, gelators **2.4** and **2.5** with the alternative meta-disubstituted aryl linkers show an opposite result. Gelator **2.5** with the longer alkyl substituents performed worse than gelator **2.4**. A total of 8 of 15 solvents gave gels or partial gels with gelator **2.4** (**Figure 13**) and 3 out of 15 solvents tested for gelator **2.5 (Table 2)**. The explanation might lie in the shorter structure of the linker and a delicate balance of lipophilicy.

A.  **B.** 

Figure 13. A. Gels of gelator **2.2** in toluene. **B.** Gels of gelator **2.4** in ethanol.

Table 2. Gel screen results of gelators **2.2**, **2.3**, **2.4** and **2.5** all in the concentration of 1% w/v. Gels prepared through traditional sonicating-heating-cooling steps and formed within a month after standing.

1% w/v	**2.2**	**2.3**	**2.4**	**2.5**
1,2,4-TCB	PG	ppt	ppt	S
1,2-DBE	S	ppt	ppt	S
2-Butanone	ppt	ppt	G	ppt
1,2-DCB	PG	S	ppt	ppt
1,4-Dioxane	ppt	PG	PG	ppt
2-Picoline	S	S	G	ppt
ACO	ppt	IS	G	ppt
ACN	ppt	ppt	PG	ppt
Benzyl Alcohol	S	S	PG	G
Chloroform	PG	S	ppt	ppt
Cyclohexane	G	IS	S	ppt
DEG	ppt	ppt	G	ppt
Ethanol	G	ppt	G	G
Toluene	PG	ppt	ppt	PG
Water	IS	IS	IS	IS

ppt-precipitate, PG-partial gel, G-gel, S-soluble, IS-insoluble.

3.2.3 Gel screen results for analogues 2.9 and 2.11

Both compounds **2.9** and **2.11** have the meta-disubstituted aryl linker and are non-gelators themselves. However, they perform well in presence of a metal centre. (Gel screen results tables are in the appendix due to the large quantities.)

For compounds **2.9** and **2.11**, Cd(II) and Cu(II) was chosen as the metal centres to help the gel formation. In De's recent paper, Cd(II) centred metallogelators have been studied.[80] In De's work, cadmium nitrates performed well in forming metallogels with N^2, N^6-bis(5-(3)-(pyridine-2-yl)-1*H*-Pyrazole-3(5)-carbonyl)-pyridine-2,6-di-carbohydrazide. In this project, chlorides and nitrates of the two metals Cd(II) and Cu(II) were both tested as part of a metallogel screen. Surprisingly that the nitrates did not perform as well as reported in previous works.[80,81] Nitrates

are preferred to chlorides because chloride is a good hydrogen bond acceptor and can interrupt the hydrogen bonding formation between the urea NH groups and the oxygen atoms of the carbonyl groups.

When doing the gel screening for compound **2.9**, crystals resulted from a solution of 4-picoline in the presence of $Cd(NO_3)_2$. However, according to the single crystal X-ray diffraction structure determination, the structure did not show the presence of Cd(II) and proved to be of the uncomplexed ligand (**Figure 14**).

The structure was reported before by Steed and co-workers.[79] The crystal system is tetragonal and the space group of the crystal is $I\bar{4}2d$. The sterically demanding spacer group and competing hydrogen bonding of compound **2.9** stop the urea tape forming. In the crystal structure, hydrogen bonds preferred a combination type of $R_2^2(10)$ and $R_2^1(6)$ (**Scheme 23**).[82] The hydrogen bonding $R_2^2(10)$ formation between the urea NH groups and the oxygen atoms of the carbonyl groups take priority in the structure as it allows the supramolecular framework aggregation and then gelation.

Further crystallisation experiments using different kinds of metal nitrates were placed in order to obtain the coordination way between the metal centre and compound **2.9** (**Table 3**). Unfortunately, the crystals found in methanol with $Co(NO_3)_2$ still cannot explain the coordination between compound **2.9** and the central metal but show a different structure which has not been reported yet with orthorhombic crystal cells with *Pbca* space group. In the newly found structure, intermolecular hydrogen bonds formed between the urea NH groups and the oxygen atoms of the carbonyl groups on the same ligand. Data of the crystal structures will be further discussed in section **5.7**.

Attempts were made to prepare complexes of cadmium (II), copper (II), cobalt (II) and nickel (II) nitrates with **2.11** using the same list of solvents in three different ways, either evaporation (addition of solvents to just dissolve the solid and allow it to evaporate at room temperature to give crystals), slow cooling (use heating to help dissolve the solid, seal the vial and allow it cool down crystallise) and anti-solvent diffusion (take advantage of another solvents which has difference of the boiling point to diffuse as a vapour into the solution in order to crystallise the product). However, no crystalline products were isolated.

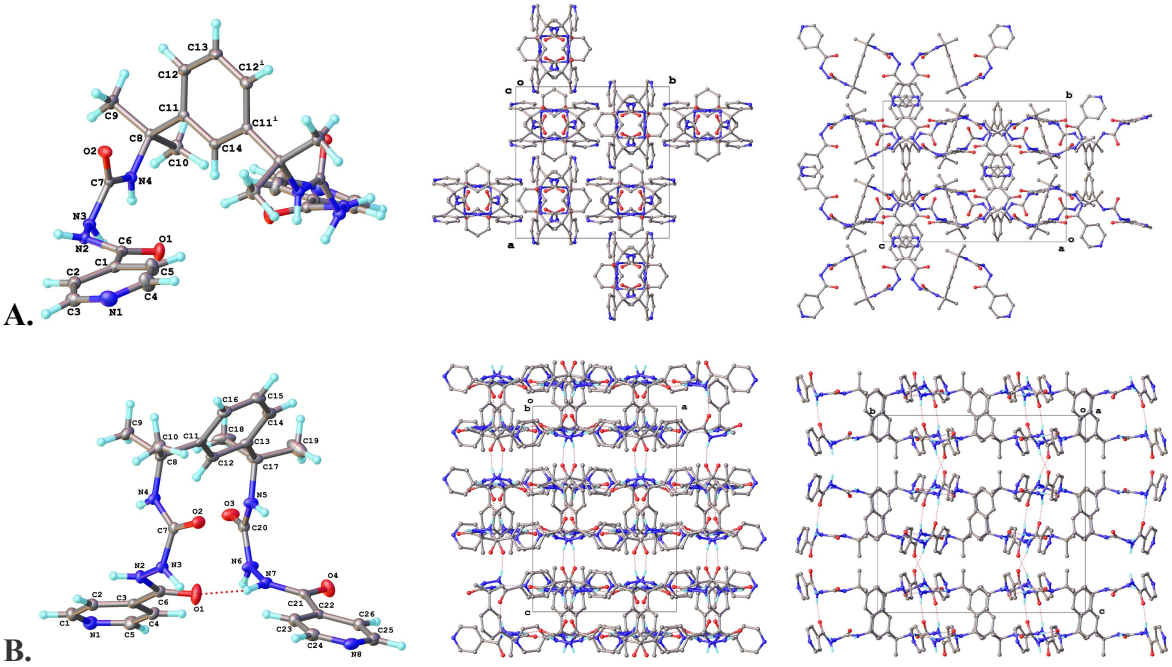
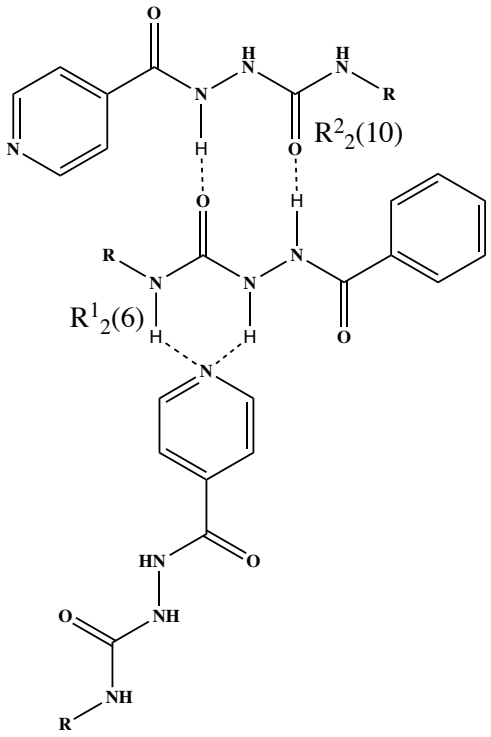


Figure 14. The crystal structures of ligand **2.9** obtained from in the presence of **A.** Cadmium nitrate and **B.** Cobalt nitrate.



Scheme 23. The mixture of hydrogen bonds in the crystal structure of compound **2.9**. The hydrogen bonding type $R^2_2(10)$ could be explained as the interactions between urea groups and forms a ten-membered ring.

Table 3. Another two different metal nitrates tried with **2.9** in order to get crystals for structures. Tiny poor quality crystals gave in methanol with $Co(NO_3)_2$ but are unable to be detected.

2.9	Methanol	Toluene	ACN	ACO	Water
$Co(NO_3)_2$	Crys.	S	S	S	ppt
$Ni(NO_3)_2$	S	S	S	S	ppt

ppt-precipitate, S-soluble, Crys.-crystallisation

3.2.4 Gel screen results for analogues 2.10 and 2.12

In previous work by Steed and co-workers[79], compound **2.10** has been found to be a good gelator which gave a plenty of gels. However, when the experiment was repeated in this project, compound **2.10** proved to be insoluble in the majority of solvents even via sonication for hours. For the purpose of dissolution, heating along with sonicating at the same time was applied to compound **2.10**. Fortunately, after the mixture of compound **2.10** in a list of solvents (**Table 4**) was sonicated at 50℃ for 5h, the majority of the mixture goes into solution and almost half of the solutions gave partial gels after cooling down to room temperature (**Table 4**).

However, compound **2.12** did not show the same good results as its analogue compound **2.10** when the same method heating and sonicating for hours was tried for it. It does not dissolve in almost every single solvent tested (**Table 5**) with only 6 exceptions. But after cooling the solutions to the room temperature, 5 of them precipitated. The only solvent that the compound proved to be soluble in at room temperature was DMSO without any formation of gels.

For both compounds **2.10** and **2.12**, complexation with copper (II) and cobalt (II) nitrates were attempted in a range of conditions for crystallisation but no single crystal has been isolated.

Table 4. The gel screen results of gelator **2.10** at 1% w/v.

1,2,4-TCB	S	3-Chloro-1-propanol	PG	DCM	ppt	NB	S
1,2-DBE	ppt	3-Picoline	S	Diethyl ether	PG	NM	ppt
2-Butanone	ppt	4-Ethyl pyridine	S	DEG	ppt	P-xylene	PG
1,2-DCB	S	4-Picoline	PG	Diisopropyl ether	S	Pyridine	ppt
1,3-DCB	S	Acetone	ppt	DMA	S	THF	PG
1,4-Dioxane	S	Acetonitrile	S	DMF	S	Toluene	ppt
1-Butanol	PG	Benzene	PG	DMSO	ppt		
1-Pentanol	ppt	Benzyl alcohol	S	Ethanol	ppt		
1-Propanol	PG	Chlorobenzene	ppt	Ethyl acetate	PG		
2-Butanol	S	Chloroform	ppt	EG	PG		
2-Ethyl pyridine	S	Cyclohexane	PG	EGBE	ppt		
2-Picoline	S	Cyclohexanone	PG	Mesitylene	S		
2-Propanol	S	Cyclopentanone	PG	Methanol	ppt		

ppt-precipitate, PG-partial gel, S-soluble.

Table 5. The gel screen results of gelator **2.12** at 1% w/v.

1,2,4-TCB	ppt.	3-Chloro-1-propanol	IS	DCM	IS	NB	IS
1,2-DBE	ppt.	3-Picoline	IS	Diethyl ether	IS	NM	IS
2-Butanone	IS	4-Ethyl pyridine	IS	DEG	IS	P-xylene	IS
1,2-DCB	ppt.	4-Picoline	IS	Diisopropyl ether	IS	Pyridine	IS
1,3-DCB	ppt.	Acetone	IS	DMA	IS	THF	IS
1,4-Dioxane	ppt.	Acetonitrile	IS	DMF	IS	Toluene	IS
1-Butanol	IS	Benzene	IS	DMSO	S		
1-Pentanol	IS	Benzyl alcohol	IS	Ethanol	IS		
1-Propanol	IS	Chlorobenzene	IS	Ethyl acetate	IS		
2-Butanol	IS	Chloroform	IS	EG	IS		
2-Ethyl pyridine	IS	Cyclohexane	IS	EGBE	IS		
2-Picoline	IS	Cyclohexanone	IS	Mesitylene	IS		
2-Propanol	IS	Cyclopentanone	IS	Methanol	IS		

ppt-precipitate, IS-insoluable.

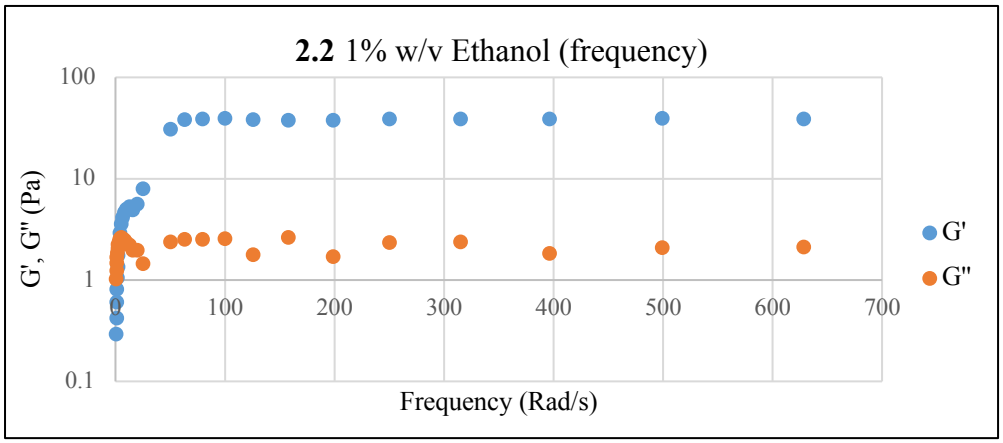
3.3 Gel rheology

The most common way to learn the physical properties of gels is rheology, first developed by Bingham in 1929.[83] It helps to know the viscosity of the gels and can locate the point when the gel breaks down. What is more, it also assists to define the supramolecular gels.[84] In rheology, there are an elastic storage modulus G' which displays the solid-like behaviour of gel and an elastic loss modulus which displays the liquid-like viscous behaviour of gel. It is commonly that G' shows to be an order of magnitude greater than G'' for a gel material while a week stress (σ) has been applied and during the weak stress applied, G' should appear as a constant over a wide range of frequencies. Upon the applied stress increasing, the gel system shears and starts flowing, G' value would go a dropping process which even below G'' value, which indicates that the gel has been broken into a liquid state.

3.3.1 Rheology results for squaramide gelators 2.2, 2.4, 2.5 and 2.6

For squaramide gelators **2.2**, **2.4** and **2.5**, several gels have been chosen to do the rheology tests at only 1% w/v due to the limit amount of compound available.

The gels of gelator **2.2** in ethanol proved to be quite weak gels which broke even upon shaking. According to the **Chart 1**, although G' stays invariant and exceed G'' in an order of magnitude in frequency spectrum which obeys the principle for supramolecular gels, [85] both G' and G'' shows in quite low magnitude which even lower than 100Pa. During rheology testing, the gel always broke down during the initial frequency step or when being transferred onto the rheometer. Since gel formation takes several days, it is impossible to prepare the gel directly on the plate of the machine.



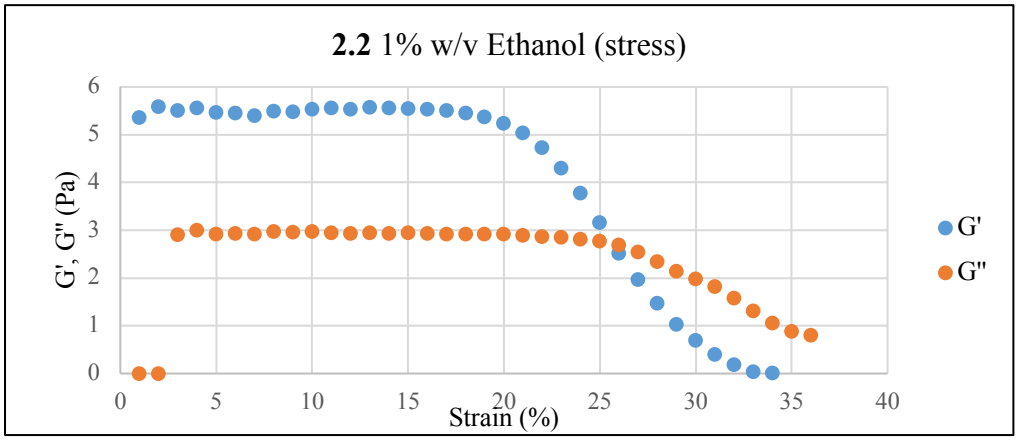
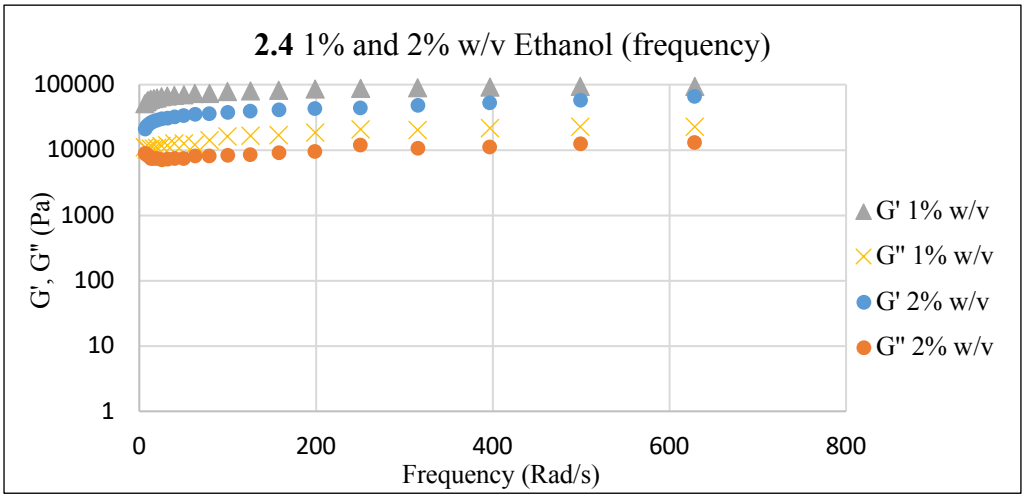


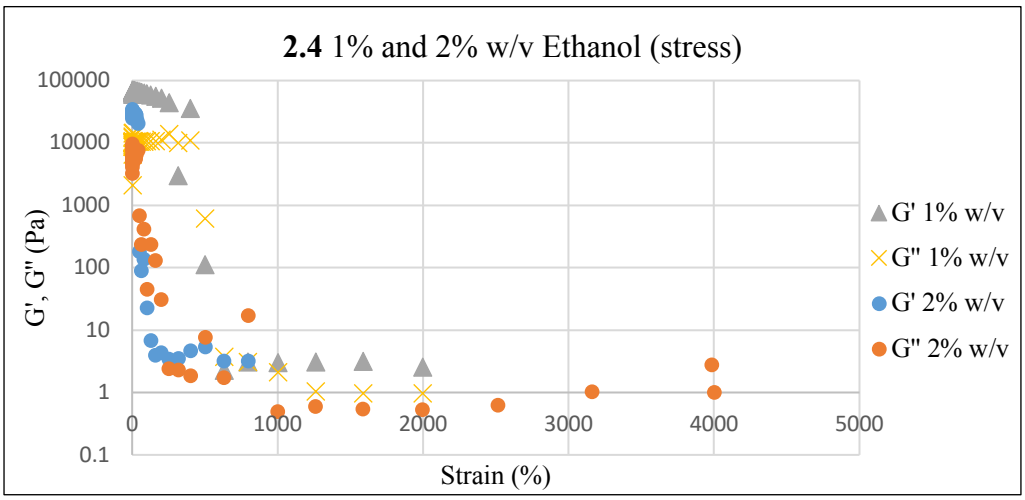
Chart 1. The rheology test for gelator **2.2** at 1% w/v.

Gels made of gelators **2.4** (**Chart 2**) and **2.5** (**Chart 3**) proved to be more robust than gelator **2.2**. G' and G'' for gelators 2.4 and 2.5 are ten thousand times higher than gelator 2.2.

For gelators **2.4**, both 1% and 2% w/v in ethanol have been tested. The 1% w/v gels showed better stability and viscosity. Over the critical strain region (γ = 73.0%), G' of 1% and 2% w/v gels reduced dramatically (**Chart 2**), 1% w/v gels broke down at 2512 Pa while the breaking point of 2% w/v gels was at 794.3 Pa.

For gelators **2.5**, only 1% w/v gels have done the rheology as the 2% w/v gelators in ethanol resulted in preticipate. The gel to sol transation for the gel of gelator **2.5** took place at 398.1 Pa, which is even much lower than the 2% w/v gels of gelator **2.4**.





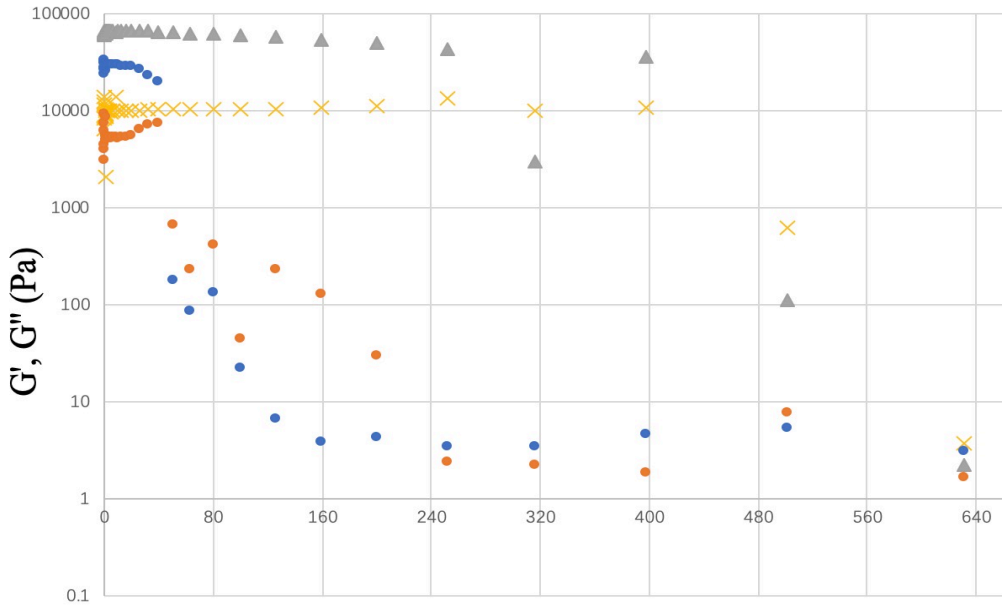


Chart 2. The rheology test for gelator **2.4** at 1% and 2% w/v in ethanol.

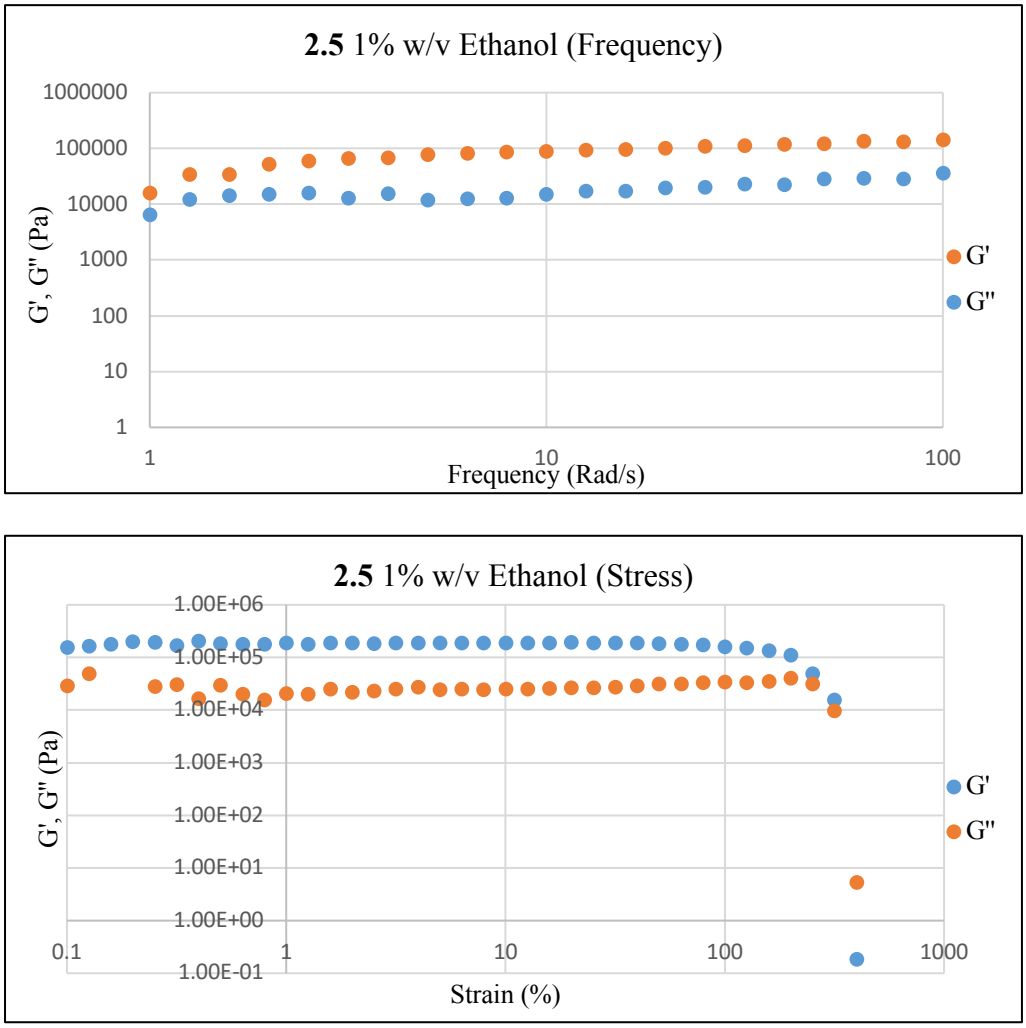


Chart 3. The rheology for gelator **2.5** at 1% w/v in ethanol.

For metallogelator **2.6** (**Chart 4**), only the gel formed in 1,2,4-TCB at 2% w/v in the presence of 0.5 equivalence $CuCl_2$ was studied by rheology because of the long time needed for gel formation and the limit amount of the gelator **2.6** purchased from Maynooth University. According to the chart, G' actually stays in a higher level than G'' which verified its identity of gel and agreed with the result from the inversion test. While the gel was carried out for the next oscillation stress step, it destroyed easily during the process which indicated the low viscosity.

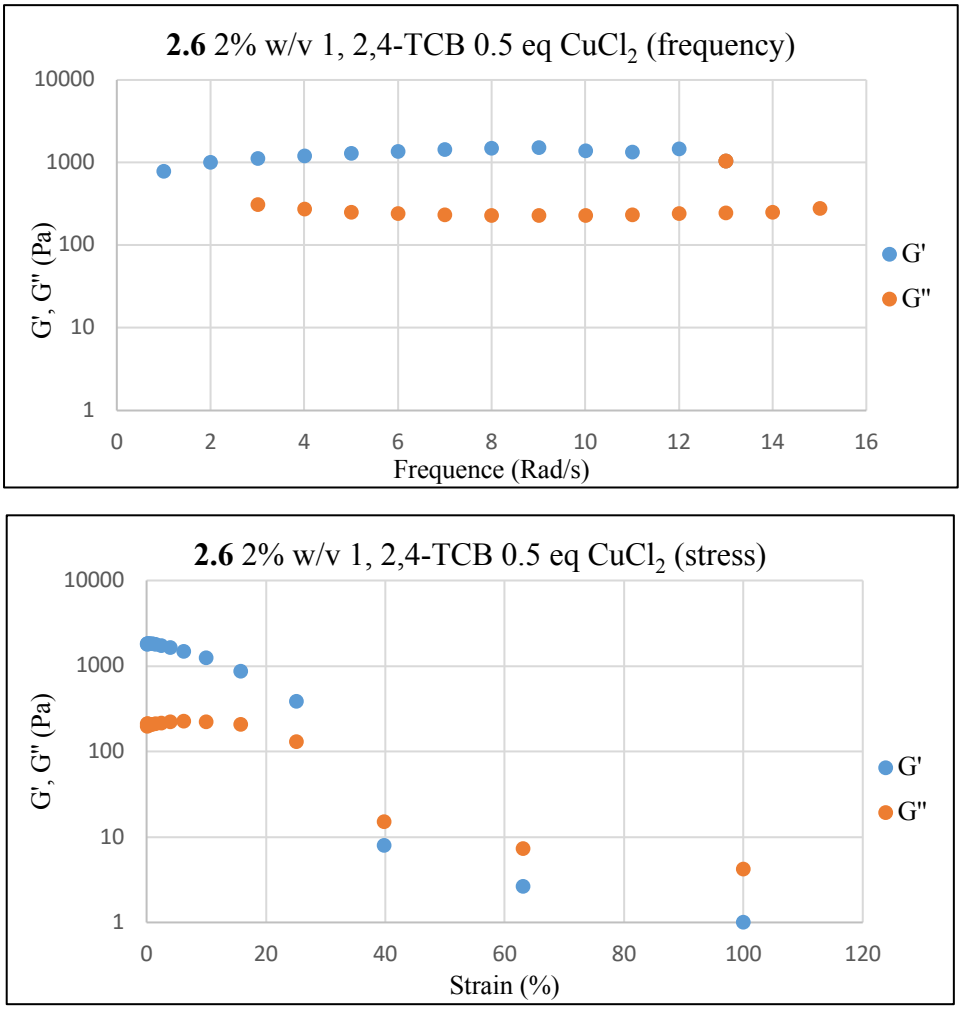
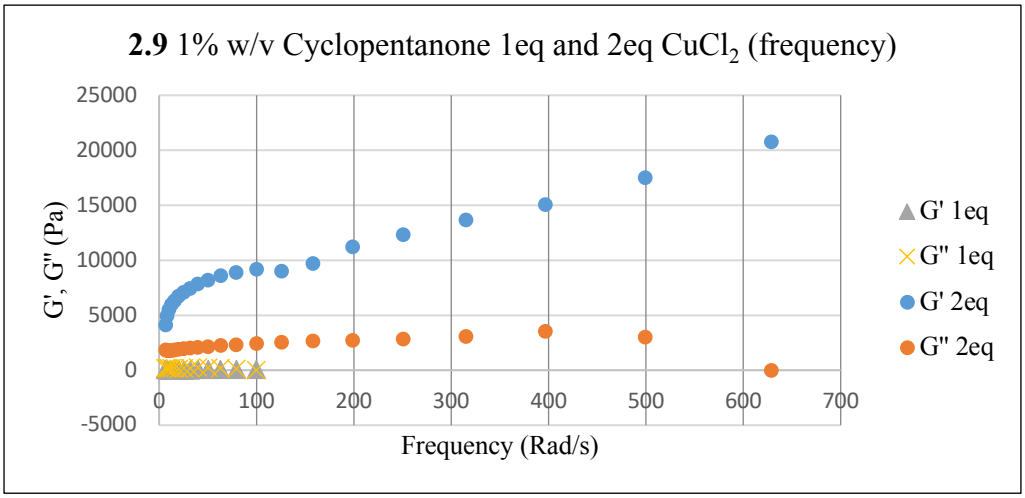


Chart 4. The rheology for gelator **2.6** at 2% w/v in the presemce of 0.5 equivalent $CuCl_2$ in 1,2,4-TCB.

3.3.2 Rheology results for analogues 2.9 and 2.11 with meta-disbstituted aryl linker

The analogues **2.9** (**Chart 5**) and **2.11** (**Chart 6**) displayed good gelation ability as metallogelators. Selected of gels at different concentrations were studied by rheology to particularly to determine the dependence of the gel properties on the metal salt.

For gelator **2.9**, when changing the equivalent of the metal with a fixed concentration of gelator, the gels with 2.0 equivalent of metal proved to have around 20 times better strength than the 1.0 equivalent gels for both viscosity and elasticity.



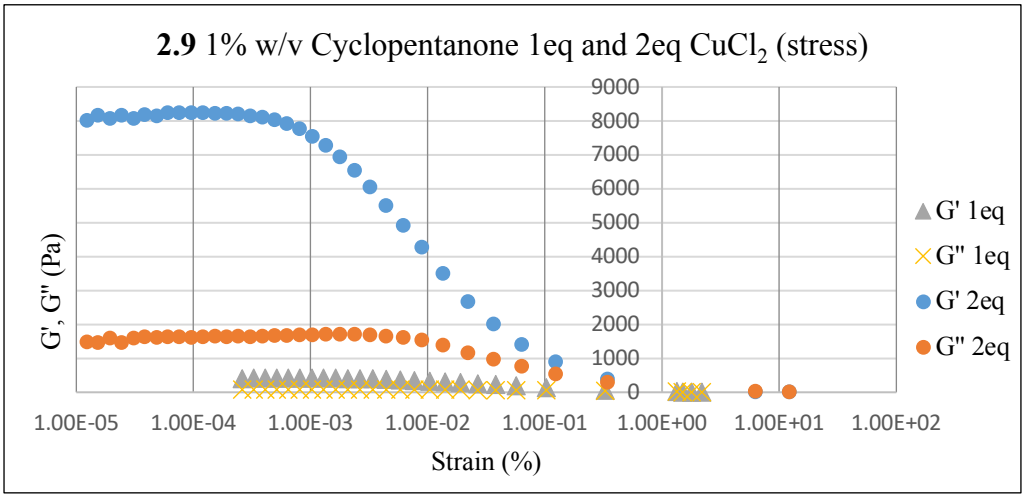


Chart 5. The rheology test for gelator **2.9** at 1% w/v in the presence of 1.0 and 2.0 equivalent of CuCl2.

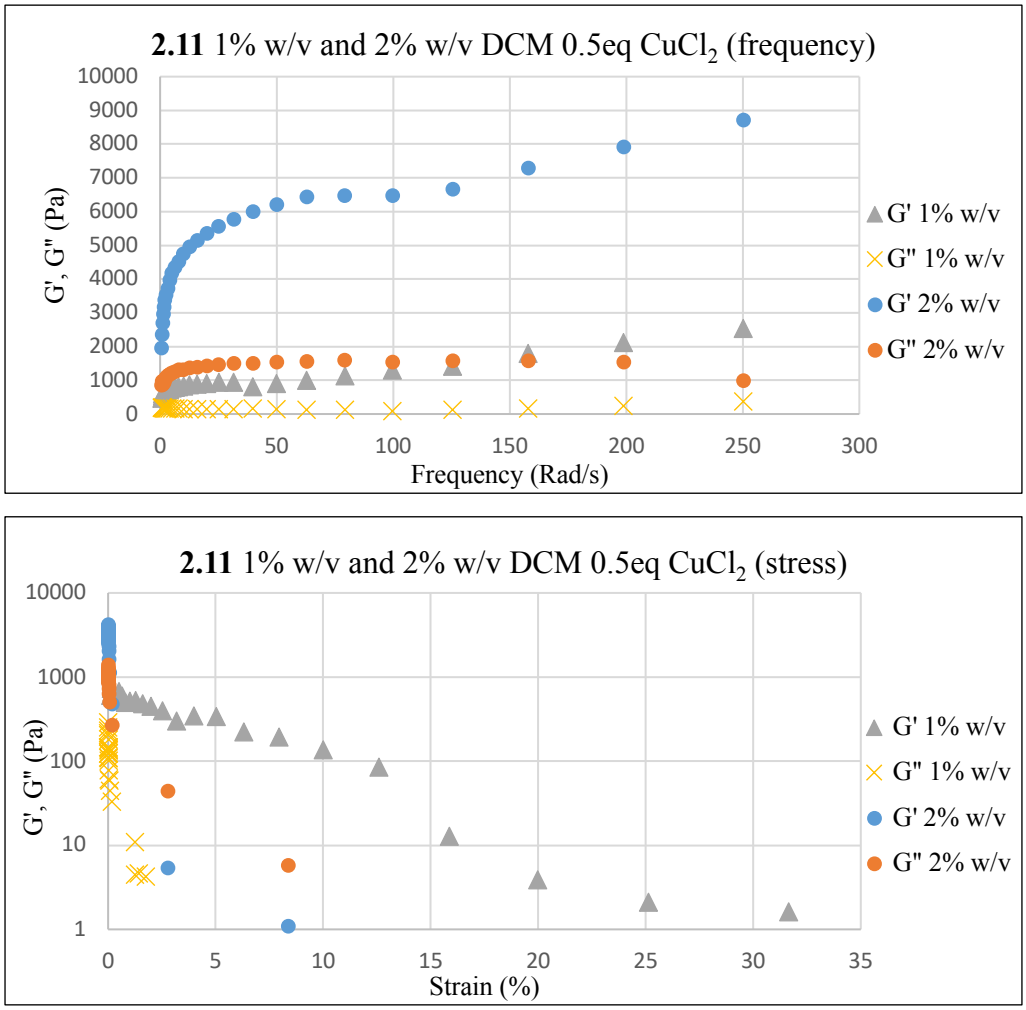


Chart 6. The rheology test for gelator **2.11** at 1% w/v and 2% w/v in the presence of 0.5 equivalence of $CuCl_2$ in DCM.

At the same time, gelator **2.11**, the concentration of gelator became the variate while the equivalence of the metal stayed the same. According to the charts, higher concentration (2% w/v) of gelator **2.11** made approximately 5 more times stronger gels than the 1% w/v gels. In comparison, the 2% w/v gels broke down at 158.5 Pa while the 1% w/v gels broke down at 19.95 Pa. However, both of the data are quite low which indicates the weakness of the gels made from gelator **2.11**.

3.3.3 Rheology results for analogues 2.10 and 2.12 with tetraethyl diphenylmethane diisocyanate linker

Rheology was attempted with **2.10** and **2.12**, even though only partial gels were found with compound **2.10** (**Chart 7**). During the experiment, a 1% w/v gel of **2.10** in benzene alcohol broke down during the frequency sweep and stress sweep measurements were not possible. As

a result, a stronger gel at 2% w/v was studied using rheology and however, it proved to be a weak gel according to the low point which transferring from gel state to sol state.

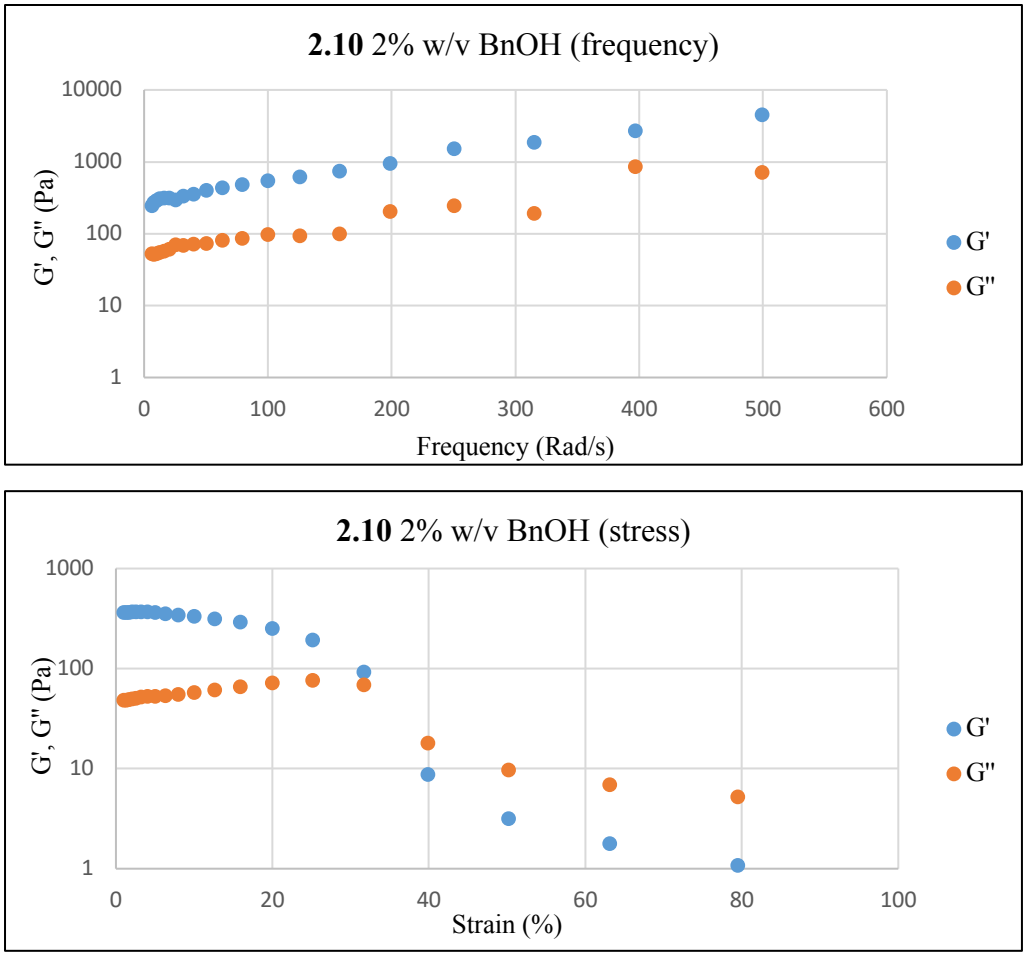


Chart 7. The rheology test for gelator **2.10** at 2% w/v.

4 Conclusions and future work

4.1 Conclusions

To sum up, squaramide based gelators **2.1**-**2.8** were prepared in collaboration with the Elmes Group at Maynooth University, while **2.9**-**2.13** were prepared as part pf this project using literature precedent or variations thereon the reaction of the amine group isoniazid or nicotinic hydrazide and a diisocynate. Compounds were characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectroscopy and elemental analysis in order to confirm the formation of these compounds comparing with the literature in the case of known compounds.

Half of the squaramides perform as non-gelators in the gel screen test, namely **2.1**,**2.3**,**2.7** while **2.8**. **2.2**, **2.4** and **2.5** formed weak clear gels by themselves. Compound **2.6** proved to be a good metallogelator with the in the presence of $CuCl_2$.

Compound **2.9** proved to be a good metallogelator with the best results obtained with 1 equivalent at 2% w/v with $CdCl_2$. Similarly, **2.11** also proved to be a metallogelator. With the most effective gels being obtained with 0.5 equivalent at 2% w/v with $CuCl_2$. These compounds are non-gelators by themselves, however. Compounds **2.10** and **2.12** proved to be quite insoluble in many of the solvents studied. Compound **2.13** was not further pursued due to time constraints and some of the gelation characteristics have already been discussed by Liu and Steed.[86]

All the gelation steps involve sonicating and heating then cooling down to the room temperature. Once the systems have been left for hours or days, a simple tube inversion experiment was carried to find out whether a gel was formed since gels should resist flow under gravity.

4.2 Future work

In this project, gelators made have been characterised by a range of analytical methods, particularly NMR spectroscopy, Mass spectrometry, elemental analysis and single crystal X-ray diffraction. The bulk of the project involved gel screening and crystallization.

According to the results, **2.2**, **2.4** and **2.5** proved to be gelators while **2.6** formed metallogels in the presence of Cu(II). All of the others **2.1**, **2.3**, **2.7** and **2.8** failed to give gels both by themselves and with metal centres. The most likely reason this failure is the poor solubility of other squaramide compounds. The next step to do for these squaramides would be to try a combination of different solvents to promote a higher solubility of the compounds.

For gelators **2.9** and **2.10** which have been previously reported.[79] SEM tests on the gela would be interesting to establish the morphology of the assemblies. It would also be very interesting to obtain single crystal X-ray crystals of metal compleses of **2.9** and of **2.10**.

Gelators **2.11** and **2.12**, which are analogues of **2.9** and **2.10**, were synthesized in a similar way to **2.9** and **2.10**. Gel screening and rheology were also undertaken for these two compounds. Again, further characterisation of the gels by SEM would be useful and insights into the gelator structure both with and without metal ions could be obtained using single crystal X-ray crystallography if suitable crystallisation conditions could be found.

5 Experimental

5.1 General experimental

Chemicals were purchased from Sigma Aldrich and Fisher Scientific and were used without any further purification. Solvents and dry acetonitrile were obtained from the university solvent store. ^{1}H NMR spectra were recorded on the both Bruker Advance III 400 spectrometer at 400MHz and using the $CDCl_3$ or DMSO-d6 as the solvent. High resolution ^{1}H NMR, ^{13}C NMR, COSY, NOESY, HMBC, HSQC spectra were all carried on Varian VNMRS-600 and VNMES-700 spectrometers. Mass spectrometer Qp2010-Ultra (Shimadzu) was used for ESI spectra. Single crystal X-ray diffraction was carried out on D8venture diffractometer (PHOTON-100 CMOS detector, IμS-microsource, focusing mirrors, MoKα, λ = 0.71073 Å) with Bruker APEX-II software.

5.2 Synthesis of tetraethyl diphenylmethane diisocyanate linker

A solution made of di-tert-butyl dicarbonate (6.008g, 27.53mmol) in dry acetonitrile (20mL) was added slowly into a solution made of 4-(dimethylamino)pyridine (0.33g, 2.72mmol) in dry acetonitrile (20mL). To the whole mixture, 4,4'-methylenebis(2,6-diethylaniline) (4.005g, 12.90mmol) dissolved in dry acetonitrile (20mL) was added. The reaction under N_2 atmosphere was left and kept stirring for 2h. Concentrated sulfuric acid (2mL) in acetonitrile (3mL) was carefully transferred to the system after 2h and the mixture was allowed to stir for further 5min. Distilled water (65mL) was poured to the solution to give a white precipitate. The solution was extracted with hexane (4×100mL) and the organic layer was reserved, followed by drying with $MgSO_4$. Rotary evaporation was used to remove the organic solvent. The resulting white solid was re-dissolved in DCM (20mL) and the solvent removed by rotary evaporation again. The final product is white solid (4.18g, 89%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 4H, ArH), 3.87 (s, 2H, CH_2), 2.70-2.64 (q, ^{3}J= 7.5 Hz, 8H, CH_2CH_3), 1.25-1.21 (t, ^{3}J = 7.5 Hz, 12H, CH_3); $^{13}C\{1H\}$ NMR (400 MHz, $CDCl_3$) δ 138.70 (C=O), 127.45 (ArC), 41.12 (CH_2), 25.69 (CH_2CH_3), 14.23 (CH_3).

5.3 Synthesis of 2.9

1,3-bis-(1-isocyanato-1-methylethyl) benzene (0.42mL, 1.82mmol) was added into a mixture of chloroform (15mL) and ethanol (1.5mL) to make a solution and followed by isoniazid (0.51g, 3.72mmol) adding to the system. After that, triethylamine (1ml, 7.17mL) was also added. The solution was allowed to stir at 80℃ with reflux for 24 hours. The product was isolated by

filteration and washed with chloroform twice to give a white solid (0.87g, 1.70mmol, 92%). ^{1}H NMR (400 MHz, DMSO-d6) δ 10.45 (d, ^{3}J = 2.5 Hz, 2H, NH), 8.74–8.72 (dd, J = 1.6 Hz, 4.44 Hz, 4H, ArH), 7.91 (d, ^{3}J = 2.5 Hz, 2H, NH), 7.76–7.74 (dd, J = 1.6 Hz, 4.46 Hz, 4H, ArH), 7.43 (s, 1H, ArH), 7.22–7.18 (m, 3H, ArH), 6.76 (s, 2H, NH), 1.58 (s, 12H, CH_3); ^{13}C{1H} NMR (600 MHz, DMSO-d6) δ 165.14 (C=O), 157.21 (C=O), 150.92 (ArC), 148.22 (ArC), 140.07 (ArC), 127.74 (ArC), 122.92 (ArC), 121.82 (ArC), 55.29 (CCH3), 30.41 (CCH3). HRMS $[M+H]^+$ m/z 519.2484 (average), 519.2468 (calculated). Elemental analysis (%) C 53.83 (60.22), H 5.09 (5.83), N 18.33 (21.61).

5.4 Synthesis of 2.10

Isoniazid (0.50g, 3.65mmol) was added to tetraethyl diphenylmethane diisocyanate linker (0.66g, 1.82mmol) in chloroform (15mL), ethanol (1.5mL) and triethylamine (1ml, 7.17mmol). The mixture was stirred under reflux at 80℃ for 24 hours. A white solid precipitate (1.03g, 1.62mmol, 89%) was filtered off and washed with chloroform. ^{1}H NMR (400 MHz, DMSO-d6) δ 10.54 (s, 2H, NH), 8.75 – 8.72 (dd, J = 1.1 Hz, 2.9 Hz, 4H, ArH), 8.19 (s, 2H, NH), 7.96 (s, 2H, NH), 7.83 (d, ^{3}J = 3.4 Hz, 4H, ArH), 6.94 (s, 4H, ArH), 3.84 (s, 2H, CH_2), 2.55 – 2.44 (m, 8H, CH_2CH_3), 1.11-1.04 (m, 12H, CH_2CH_3); ^{13}C{1H} NMR (600 MHz, DMSO-d6) δ 165.23 (C=O), 150.62 (ArC), 140.30 (ArC), 140.16 (ArC), 131.98 (ArC), 126.63 (ArC), 121.97 (ArC), 46.16 (CH_2CH_3), 24.77 (CH_2CH_3), 15.23 (CH_3). HRMS $[M+H]^+$ m/z 637.3260 (average), 637.3251 (calculated). Elemental analysis (%) C 61.15 (66.22), H 5.91 (6.33), N 15.58 (17.60).

5.5 Synthesis of 2.11

Nicotinic hydrazide (0.50g, 3.65mmol) was placed into a mixture made of 1,3-bis-(1-isocyanato-1-methylethyl) benzene (0.42mL, 1.82mmol) in chloroform (15mL) and ethanol (1.5mL). Triethylamine (1ml, 7.17mmol) added into the solution. The reaction was carried out at 80℃ with reflux and stirring. The product was isolated by filtration as a white precipitate (0.82g, 1.58mmol, 87%) and washed with chloroform. ^{1}H NMR (400 MHz, DMSO-d6) δ 10.34 (s, 2H, NH), 9.02–8.99 (dd, J = 0.9 Hz, 2.3 Hz, 2H, NH), 8.73-8.70 (dd, J = 1.6 Hz, 4.8 Hz, 2H, NH), 8.22-8.17 (td, J = 1.9 Hz, 8.3 Hz, 2H, ArH), 7.89 (s, 2H, ArH), 7.54–7.49 (ddd, J = 0.8 Hz, 7.9 Hz, 12.7 Hz, 2H, ArH), 7.45 (s, 1H, ArH), 7.23-7.19 (m, 3H, ArH), 6.75 (s, 2H, ArH), 1.59 (s, 12H, CH_3); ^{13}C{1H} NMR (600 MHz, DMSO-d6) δ 165.34 (C=O), 157.34 (C =O), 152.69 (ArC), 148.88 (ArC), 148.24 (ArC), 135.55 (ArC), 128.71 (ArC), 127.73 (ArC), 122.91

(ArC), 121.92 (ArC), 55.28 (CCH3), 30.43 (CCH3). HRMS $[M+H]^+$ m/z 519.2470 (average), 519.2468 (calculated). Elemental analysis (%) C 59.18 (60.22), H 5.73 (5.83), N 20.92 (21.61).

5.6 Synthesis of 2.12

Nicotinic hydrozide (0.50g, 3.65mmol) was added into a mixture which tetraethyl diphenylmethane diisocyanate linker (0.66g, 1.82mmol) dissolved in chloroform (15mL) and ethanol (1.5mL), followed by the addition of triethylamine (1mL, 7.17mmol). The solution was stirred at 80℃ for 24 hours. The white solid product was isolated by filtration (1.01g, 1.59mmol, 87.21%) and washed with chloroform. ^{1}H NMR (400 MHz, DMSO-d6) δ 10.44 (s, 2H, NH), 9.04 (s, 2H, NH), 8.70-8.68 (dd, J = 1.1 Hz, 3.3 Hz, 2H, NH), 8.23-8.21 (d, 2H, ^3J =5.2 Hz, ArH), 8.12 (s, 2H, ArH), 7.93 (s, 2H, ArH), 7.51-7.48 (dd, J = 2.1 Hz, 5.4 Hz, 2H, ArH) 6.90 (s, 4H, ArH), 3.81 (s, 2H, CH_2), 2.50 – 2.41 (m, 8H, CH_2CH_3), 1.07-1.03 (t, J = 5.1 Hz, 12H, CH_2CH_3); ^{13}C{1H} NMR (600 MHz, DMSO-d6) δ 152.63 (C=O), 149.14 (ArC), 142.65 (ArC), 140.01 (ArC), 135.79 (ArC), 128.89 (ArC), 126. 60 (ArC), 123.85 (ArC), 41.14 (CH_2CH_3), 24.76 (CH_2CH_3), 15.22 (CH_3). HRMS $[M+H]^+$ m/z 637.3268 (average), 637.3251 (calculated). Elemental analysis (%) C 63.83 (66.22), H 6.22 (6.33), N 15.97 (17.60).

5.7 Explanation for error on elemental analysis

To conclude all the elemental analysis data obtained above, the discrepancy on the percent carbon might arise from the chloroform solvent. Re-calculation of the elemental analysis data to account for varying amounts of residual chloroform yields more reasonable results (**Table 6**).

Table 6. Re-calculated elemental analysis data in the presence of chloroform. Expected weight % values are in red.

Compounds	Elemental analysis
2.9 with 0.6 chloroform	C 53.83 (54.16), H 5.09 (5.19), N 18.33 (19.01)
2.10 with 0.5 chloroform	C 61.15 (61.21), H 5.91 (5.82), N 15.58 (16.09)
2.11	C 59.18 (60.22), H 5.73 (5.83), N 20.92 (21.61)
2.12 with 0.25 chloroform	C 63.83 (63.49), H 6.22 (6.04), N 15.97 (16.81)

5.8 Synthesis of 2.13

A mixture of nicotinic acid (0.37g, 3.00mmol) and triethylamine (0.46mL, 3.30mmol) was stirred in anhydrous toluene (40mL) for 45 minutes at room temperature. Then DPPA (3.60mmol) was added and the mixture heated up to 40℃ for 1 hour and then refluxed for a further 3 hours. After the solution has cooled to the room temperature, 4,4'-methylenebis(2,6-diethylaniline) (0.93g, 3.00mmol) was added and the mixture refluxed for 10 hours. The solution was then cooled to the room temperature and the solvent removed by rotary evaporation to give the crude product. Finally, methanol (50mL) was used to dissolve the crude product and by refluxing for 30 minutes and then cooled to room temperature and the white solid product isolated by filtration. (1.42g, 2.58mmol, 86%) ^{1}H NMR (400 MHz, DMSO-d6) δ 8.96 (s, 2H, NH), 8.59 (d, ^{3}J = 2.6 Hz, 2H, NH), 8.15-8.12 (dd, J = 1.46 Hz, 4.66 Hz, 2H, ArH), 7.94-7.90 (td, 2H, J = 2.05 Hz, 6.89 Hz, ArH), 7.72 (s, 2H, ArH), 7.29-7.24 (q, 2H, J = 4.33 Hz, ArH), 7.02 (s, 4H, ArH), 3.87 (s, 2H, CH_2), 2.59 – 2.52 (m, 8H, CH_2CH_3), 1.16-1.08 (t, J = 7.54 Hz, 12H, CH_2CH_3); ^{13}C{1H} NMR (600 MHz, DMSO-d6) δ 162.12 (C=O), 142.77 (ArC), 142.35 (ArC), 140.90 (ArC), 137.50 (ArC), 126. 74 (ArC), 123.95 (ArC), 40.33 (CH_2CH_3), 24.90 (CH_2CH_3), 15.12 (CH_3).

5.9 Single crystal X-ray diffraction

A Bruker D8Venture diffractometer (PHOTON-100 CMOS detector, IμS-microsource, focusing mirrors, MoKα, λ = 0.71073 Å) with Bruker APEX-II software was used to collect single crystal data for **2.9** at 120K. Crystal were prepared from a mixture of the ligand either in water with $Cd(NO_3)_2$ or in methanol with $Co(NO_3)_2$ by slow evaporation. These two crystallizations resulted in crystals only of the pure ligand in two different polymorphic forms without metal incorporation.

The crystal data for **2.9** from water with $Cd(NO_3)_2$, $C_{26}H_{30}N_8O_4$, M = 518.58, crystal size 0.35 × 0.27 × 0.15 mm^3, tetragonal, $I\bar{4}2d$ (No. 122) space group, a = b = 15.8133 (5) Å, c = 20.5773 (8) Å, V = 5145.6 (4) Å^3, Z = 8, Dc = 1.339 g cm^{-3}, μ = 0.094 mm^{-1}, $F(000)$ = 2192.0. Within the 41617 collected reflections, 3749 were found to be unique (R_{int} = 0.0416), no restraints, 233 parameters. Final GOOF = 1.040, R_1 = 0.0329 $(I>=2\sigma(I))$, wR_2 = 0.0814 (all data).

The second polymorph of **2.9** was crystallised from methanol in the presence of $Co(NO_3)_2$, $C_{26}H_{30}N_8O_4$, M = 518.58, crystal size 0.19 × 0.10 × 0.06 mm^3, orthorhombic, *Pbca* (No. 61)

space group, a = 13.3234 (19) Å, b = 20.065 (3) Å, c = 19.091 (3) Å, V = 5103.8 (12) Å^3, Z = 8, Dc = 1.350 g cm^{-3}, μ = 0.095 mm^{-1}, $F(000)$ = 2192.0. Within the 94805 collected reflections, 6166 were found to be unique (R_{int} = 0.1339), no restraints, 371 parameters. Final GOOF = 1.003, R_1 = 0.0480 $(I>=2\sigma(I))$, wR_2 = 0.1009 (all data).

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7 Appendices

Tables for gel screen results of gelators 2.9 with meta-disbstituted aryl linker in the presence of metal solution.

Table 7. The gel screen results of **2.9** at 1% w/v in the presence of 0.5 equivalence of $CdCl_2$ which gives one-third of the solvent list partial gels.

$CdCl_2$	0.5eq	$CdCl_2$	0.5eq	$CdCl_2$	0.5eq	$CdCl_2$	0.5eq
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	ppt
1,2-DBE	ppt	3-Picoline	S	DEG	G	O-xylene	ppt
2-Butanone	PG	4-Picoline	Crys.	Diisopropyl ether	PG	P-xylene	ppt
1,2-DCB	ppt	Acetone	PG	DMA	S	Pyridine	S
1,3-DCB	ppt	Acetonitrile	PG	DMF	S	THF	PG
1,4-Dioxane	PG	Benzene	ppt	DMSO	S	Toluene	ppt
1-Butanol	PG	Benzyl alcohol	G	Ethanol	PG	Water	Crys.
1-Pentanol	PG	Chlorobenzene	ppt	Ethyl acetate	PG		.
1-Propanol	PG	Chloroform	ppt	EG	S		
2-Butanol	PG	Cyclohexane	Crys.	EGBE	PG		
2-Ethyl pyridine	S	Cyclohexanone	PG	Mesitylene	ppt		
2-Picoline	Crys.	Cyclopentanone	PG	Methanol	G		
2-Propanol	PG	DCM	ppt	NB	ppt	1%w/v	

Table 8. The gel screen results of **2.9** at 2% w/v in the presence of 0.5 equivalence of $CdCl_2$, this attempt shows that the concentration of **2.9** in the solvents would give positive affect to the gel formation when the metal solution proportion maintains at the same level.

$CdCl_2$	**0.5eq**	**$CdCl_2$**	**0.5eq**	**$CdCl_2$**	**0.5eq**	**$CdCl_2$**	**0.5eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	DCM	ppt	NB	ppt
1,2-DBE	ppt	3-Picoline	S	Diethyl ether	ppt	NM	PG
2-Butanone	PG	4-Ethyl pyridine	S	DEG	G	O-xylene	ppt
1,2-DCB	ppt	4-Picoline	Crys.	Diisopropyl ether	ppt	P-xylene	ppt
1,3-DCB	ppt	Acetone	G	DMA	S	Pyridine	S
1,4- Dioxane	PG	Acetonitrile	G	DMF	ppt	THF	G
1-Butanol	PG	Benzene	ppt	DMSO	S	Toluene	ppt
1-Pentanol	PG	Benzyl alcohol	PG	Ethanol	G	Water	ppt
1-Propanol	PG	Chlorobenzene	ppt	Ethyl acetate	PG		
2-Butanol	PG	Chloroform	ppt	EG	PG		
2-Ethyl pyridine	ppt	Cyclohexane	ppt	EGBE	G		
2-Picoline	Crys.	Cyclohexanone	PG	Mesitylene	ppt		
2-Propanol	PG	Cyclopentanone	PG	Methanol	G	2% w/v	

Table 9. The gel screen results of **2.9** at 1% w/v in the presence of 1.0 equivalence of $CdCl_2$, keeping the concentration of the **2.9** and adding more metal solution turns out to be a good idea which forms more gels.

$CdCl_2$	**1.0eq**	**$CdCl_2$**	**1.0eq**	**$CdCl_2$**	**1.0eq**	**$CdCl_2$**	**1.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	DCM	ppt	NB	ppt
1,2-DBE	ppt	3-Picoline	S	Diethyl ether	ppt	NM	PG
2-Butanone	PG	4-Ethyl pyridine	S	DEG	G	O-xylene	ppt
1,2-DCB	ppt	4-Picoline	S	Diisopropyl ether	ppt	P-xylene	ppt
1,3-DCB	ppt	Acetone	PG	DMA	S	Pyridine	S
1,4- Dioxane	G	Acetonitrile	PG	DMF	S	THF	G
1-Butanol	PG	Benzene	ppt	DMSO	S	Toluene	ppt
1-Pentanol	PG	Benzyl alcohol	G	Ethanol	PG	Water	ppt
1-Propanol	G	Chlorobenzene	ppt	Ethyl acetate	PG		
2-Butanol	PG	Chloroform	ppt	EG	ppt		
2-Ethyl pyridine	S	Cyclohexane	ppt	EGBE	G		
2-Picoline	Crys.	Cyclohexanone	PG	Mesitylene	ppt		
2-Propanol	PG	Cyclopentanone	PG	Methanol	PG	1% w/v	

Table 10. The gel screen results of **2.9** at 2% w/v in the presence of 1.0 equivalence of $CdCl_2$, in this case, **2.9** made the best performance among all other conditions which gelled almost half of the list of solvents.

$CdCl_2$	**1.0eq**	**$CdCl_2$**	**1.0eq**	**$CdCl_2$**	**1.0eq**	**$CdCl_2$**	**1.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	PG	DCM	ppt	NB	ppt
1,2-DBE	ppt	3-Picoline	S	Diethyl ether	ppt	NM	PG
2-Butanone	PG	4-Ethyl pyridine	S	DEG	G	O-xylene	ppt
1,2-DCB	ppt	4-Picoline	S	Diisopropyl ether	ppt	P-xylene	ppt
1,3-DCB	ppt	Acetone	G	DMA	S	Pyridine	ppt
1,4- Dioxane	G	Acetonitrile	G	DMF	PG	THF	G
1-Butanol	G	Benzene	ppt	DMSO	S	Toluene	ppt
1-Pentanol	G	Benzyl alcohol	G	Ethanol	G	Water	ppt
1-Propanol	PG	Chlorobenzene	ppt	Ethyl acetate	PG		
2-Butanol	PG	Chloroform	ppt	EG	ppt		
2-Ethyl pyridine	ppt	Cyclohexane	ppt	EGBE	G		
2-Picoline	Crys.	Cyclohexanone	PG	Mesitylene	ppt		
2-Propanol	G	Cyclopentanone	PG	Methanol	G	2% w/v	

Table 11. The gel screen results of **2.9** at 1% w/v in the presence of 2.0 equivalence of $CdCl_2$, when the equivalence of metal solution continued going up, the gelation skill of **2.9** stayed quite steady.

$CdCl_2$	**2.0eq**	**$CdCl_2$**	**2.0eq**	**$CdCl_2$**	**2.0eq**	**$CdCl_2$**	**2.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	DCM	ppt	NB	ppt
1,2-DBE	ppt	3-Picoline	S	Diethyl ether	ppt	NM	ppt
2-Butanone	PG	4-Ethyl pyridine	S	DEG	G	O-xylene	ppt
1,2-DCB	ppt	4-Picoline	S	Diisopropyl ether	ppt	P-xylene	ppt
1,3-DCB	ppt	Acetone	PG	DMA	S	Pyridine	S
1,4- Dioxane	G	Acetonitrile	PG	DMF	S	THF	PG
1-Butanol	G	Benzene	ppt	DMSO	S	Toluene	ppt
1-Pentanol	G	Benzyl alcohol	G	Ethanol	PG	Water	S
1-Propanol	PG	Chlorobenzene	ppt	Ethyl acetate	PG		
2-Butanol	PG	Chloroform	ppt	EG	ppt		
2-Ethyl pyridine	S	Cyclohexane	ppt	EGBE	PG		
2-Picoline	S	Cyclohexanone	PG	Mesitylene	ppt		
2-Propanol	PG	Cyclopentanone	G	Methanol	PG	1% w/v	

Table 12. The gel screen results of **2.9** at 2% w/v in the presence of 2.0 equivalence of $CdCl_2$, some of the partial gels went into gels while the concentration of **2.9** increased.

$CdCl_2$	**2.0eq**	**$CdCl_2$**	**2.0eq**	**$CdCl_2$**	**2.0eq**	**$CdCl_2$**	**2.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	DCM	ppt	NB	ppt
1,2-DBE	ppt	3-Picoline	S	Diethyl ether	ppt	NM	PG
2-Butanone	G	4-Ethyl pyridine	S	DEG	G	O-xylene	ppt
1,2-DCB	ppt	4-Picoline	Crys.	Diisopropyl ether	PG	P-xylene	ppt
1,3-DCB	ppt	Acetone	G	DMA	S	Pyridine	s
1,4- Dioxane	G	Acetonitrile	G	DMF	ppt	THF	G
1-Butanol	G	Benzene	ppt	DMSO	S	Toluene	ppt
1-Pentanol	G	Benzyl alcohol	PG	Ethanol	G	Water	ppt
1-Propanol	G	Chlorobenzene	ppt	Ethyl acetate	PG		
2-Butanol	PG	Chloroform	ppt	EG	PG		
2-Ethyl pyridine	ppt	Cyclohexane	ppt	EGBE	G		
2-Picoline	Crys.	Cyclohexanone	PG	Mesitylene	ppt		
2-Propanol	PG	Cyclopentanone	PG	Methanol	G	2% w/v	

Table 13. The gel screen results of **2.9** at 1% w/v in the presence of 0.5 of $Cd(NO_3)_2$.

$Cd(NO_3)_2$	**0.5eq**	**$Cd(NO_3)_2$**	**0.5eq**	**$Cd(NO_3)_2$**	**0.5eq**	**$Cd(NO_3)_2$**	**0.5eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	ppt
1,2-DBE	ppt	3-Picoline	S	DEG	ppt	P-xylene	ppt
2-Butanone	ppt	4-Picoline	S	Diisopropyl ether	ppt	Pyridine	S
1,2-DCB	ppt	Acetone	S	DMA	-	THF	S
1,3-DCB	ppt	Acetonitrile	S	DMF	S	Toluene	ppt
1,4- Dioxane	S	Benzene	ppt	DMSO	S	Water	ppt
1-Butanol	S	Benzyl alcohol	S	Ethanol	ppt		
1-Pentanol	S	Chlorobenzene	ppt	Ethyl acetate	ppt		
1-Propanol	S	Chloroform	ppt	EG	S		
2-Butanol	S	Cyclohexane	ppt	EGBE	S		
2-Ethyl pyridine	-	Cyclohexanone	S	Mesitylene	ppt		
2-Picoline	ppt	Cyclopentanone	S	Methanol	S		
2-Propanol	S	DCM	ppt	NB	ppt	1% w/v	

Table 14. The gel screen results of **2.9** at 2% w/v in the presence of 0.5 equivalence of $Cd(NO_3)_2$.

$Cd(NO_3)_2$	**0.5eq**	**$Cd(NO_3)_2$**	**0.5eq**	**$Cd(NO_3)_2$**	**0.5eq**	**$Cd(NO_3)_2$**	**0.5eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	ppt
1,2-DBE	ppt	3-Picoline	S	DEG	ppt	P-xylene	ppt
2-Butanone	ppt	4-Picoline	S	Diisopropyl ether	ppt	Pyridine	S
1,2-DCB	ppt	Acetone	S	DMA	-	THF	S
1,3-DCB	ppt	Acetonitrile	S	DMF	S	Toluene	ppt
1,4- Dioxane	S	Benzene	ppt	DMSO	S	Water	ppt
1-Butanol	ppt	Benzyl alcohol	ppt	Ethanol	ppt		
1-Pentanol	ppt	Chlorobenzene	ppt	Ethyl acetate	ppt		
1-Propanol	ppt	Chloroform	ppt	EG	S		
2-Butanol	S	Cyclohexane	ppt	EGBE	ppt		
2-Ethyl pyridine	-	Cyclohexanone	ppt	Mesitylene	ppt		
2-Picoline	S	Cyclopentanone	S	Methanol	ppt		
2-Propanol	S	DCM	ppt	NB	ppt	2% w/v	

Table 15. The gel screen results of **2.9** at 1% w/v in the presence of 1.0 equivalence of $Cd(NO_3)_2$, crystals gained in acetone with poor quality.

$Cd(NO_3)_2$	**1.0eq**	**$Cd(NO_3)_2$**	**1.0eq**	**$Cd(NO_3)_2$**	**1.0eq**	**$Cd(NO_3)_2$**	**1.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	DCM	ppt	NB	ppt
1,2-DBE	ppt	3-Picoline	ppt	Diethyl ether	ppt	NM	ppt
2-Butanone	ppt	4-Ethyl pyridine	S	DEG	S	O-xylene	ppt
1,2-DCB	ppt	4-Picoline	S	Diisopropyl ether	ppt	P-xylene	ppt
1,3-DCB	ppt	Acetone	Crys.	DMA	S	Pyridine	ppt
1,4- Dioxane	S	Acetonitrile	ppt	DMF	S	THF	S
1-Butanol	S	Benzene	ppt	DMSO	S	Toluene	ppt
1-Pentanol	S	Benzyl alcohol	ppt	Ethanol	ppt	Water	ppt
1-Propanol	S	Chlorobenzene	ppt	Ethyl acetate	ppt		
2-Butanol	S	Chloroform	ppt	EG	S		
2-Ethyl pyridine	S	Cyclohexane	ppt	EGBE	S		
2-Picoline	ppt	Cyclohexanone	ppt	Mesitylene	ppt		
2-Propanol	S	Cyclopentanone	S	Methanol	ppt	1% w/v	

Table 16. The gel screen results of **2.9** at 2% w/v in the presence of 1.0 equivalence of $Cd(NO_3)_2$.

$Cd(NO_3)_2$	**1.0eq**	**$Cd(NO_3)_2$**	**1.0eq**	**$Cd(NO_3)_2$**	**1.0eq**	**$Cd(NO_3)_2$**	**1.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	DCM	ppt	NB	ppt
1,2-DBE	ppt	3-Picoline	ppt	Diethyl ether	ppt	NM	ppt
2-Butanone	ppt	4-Ethyl pyridine	S	DEG	ppt	O-xylene	ppt
1,2-DCB	ppt	4-Picoline	ppt	Diisopropyl ether	ppt	P-xylene	ppt
1,3-DCB	ppt	Acetone	ppt	DMA	S	Pyridine	ppt
1,4- Dioxane	ppt	Acetonitrile	ppt	DMF	S	THF	S
1-Butanol	ppt	Benzene	ppt	DMSO	S	Toluene	ppt
1-Pentanol	ppt	Benzyl alcohol	S	Ethanol	ppt	Water	ppt
1-Propanol	ppt	Chlorobenzene	ppt	Ethyl acetate	ppt		
2-Butanol	ppt	Chloroform	ppt	EG	ppt		
2-Ethyl pyridine	ppt	Cyclohexane	ppt	EGBE	ppt		
2-Picoline	ppt	Cyclohexanone	ppt	Mesitylene	ppt		
2-Propanol	ppt	Cyclopentanone	S	Methanol	ppt	2% w/v	

Table 17. The gel screen results of **2.9** at 1% w/v and 2% w/v in the presence of 0.5, 1.0 and 2.0 equivalence of $CuCl_2$ and $Cu(NO_3)_2$, it is obviously that $CuCl_2$ solution helps more during the formation of the supramolecular network and when the **2.9** concentrated from 1% w/v to 2% w/v, more gels formed.

1% w/v	**Equivalence**	**MeOH**	**$CHCl_3$**	**Tol.**	**Chlorobenzene**	**Hexane**	**ACN**
Solubility							
CuCl2	0.5	S	IS	PG	S	PG	PG
Cu(NO3)2	0.5	S	IS	IS	S	S	PG
CuCl2	1	S	IS	IS	PG	PG	PG
Cu(NO3)2	1	S	IS	IS	S	S	S
CuCl2	2	PG	W	IS	PG	PG	G
Cu(NO3)2	2	S	W	IS	S	S	S

2% w/v	**Equivalence**	**MeOH**	**$CHCl_3$**	**Tol.**	**Chlorobenzene**	**Hexane**
Solubility						
CuCl2	0.5	PG	G	PG	S	PG
Cu(NO3)2	0.5	S	IS	PG	S	S
CuCl2	1	G	IS	IS	PG	G
Cu(NO3)2	1	IS	IS	IS	S	S
CuCl2	2	G	W	IS	PG	G
Cu(NO3)2	2	IS	W	IS	S	S

Tables for gel screen results of gelators 2.11 with meta-disbstituted aryl linker in the presence of metal solution.

Table 18. The gel screen results of **2.11** at 1% w/v in the presence of 0.5 equivalence of $CdCl_2$, which did not perform as well as 2.9 but there still formed some partial gels and gels.

$CdCl_2$	**0.5eq**	$CdCl_2$	**0.5eq**	$CdCl_2$	**0.5eq**	$CdCl_2$	**0.5eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	ppt
1,2-DBE	ppt	3-Picoline	S	DEG	PG	P-xylene	ppt
2-Butanone	ppt	4-Picoline	S	Diisopropyl ether	ppt	Pyridine	S
1,2-DCB	ppt	Acetone	PG	DMA	S	THF	S
1,3-DCB	ppt	Acetonitrile	G	DMF	S	Toluene	PG
1,4-Dioxane	S	Benzene	ppt	DMSO	S	Water	ppt
1-Butanol	ppt	Benzyl alcohol	PG	Ethanol	G		
1-Pentanol	ppt	Chlorobenzene	ppt	Ethyl acetate	S		
1-Propanol	S	Chloroform	ppt	EG	ppt		
2-Butanol	S	Cyclohexane	ppt	EGBE	S		
2-Ethyl pyridine	PG	Cyclohexanone	PG	Mesitylene	ppt		
2-Picoline	PG	Cyclopentanone	PG	Methanol	ppt		
2-Propanol	S	DCM	ppt	NB	ppt	1% w/v	

Table 19. The gel screen results of **2.11** at 2% w/v in the presence of 0.5 equivalence of $CdCl_2$, better performance gained when the concentration of **2.11** raised, according to the table, nearly half of the solvents partial gelled or gelled.

$CdCl_2$	**0.5eq**	$CdCl_2$	**0.5eq**	$CdCl_2$	**0.5eq**	$CdCl_2$	**0.5eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	PG	NM	ppt
1,2-DBE	ppt	3-Picoline	Crys.	DEG	PG	P-xylene	ppt
2-Butanone	PG	4-Picoline	S	Diisopropyl ether	ppt	Pyridine	S
1,2-DCB	ppt	Acetone	G	DMA	S	THF	S
1,3-DCB	ppt	Acetonitrile	G	DMF	S	Toluene	ppt
1,4-Dioxane	S	Benzene	ppt	DMSO	S	Water	ppt
1-Butanol	PG	Benzyl alcohol	PG	Ethanol	PG		
1-Pentanol	PG	Chlorobenzene	ppt	Ethyl acetate	ppt		
1-Propanol	PG	Chloroform	ppt	EG	G		
2-Butanol	PG	Cyclohexane	PG	EGBE	PG		
2-Ethyl pyridine	PG	Cyclohexanone	PG	Mesitylene	ppt		
2-Picoline	PG	Cyclopentanone	PG	Methanol	G		
2-Propanol	G	DCM	ppt	NB	ppt	2% w/v	

Table 20. The gel screen results of **2.11** at 1% w/v in the presence of 0.5 equivalence of $CuCl_2$, compared with $CdCl_2$, $CuCl_2$ did not show to be the same good for the formation of supramolecular network. But transparent partial gels(TPG) and transparent gels(TG) obtained.

$CuCl_2$	**0.5eq**	**$CuCl_2$**	**0.5eq**	**$CuCl_2$**	**0.5eq**	**$CuCl_2$**	**0.5eq**
1,2,4-TCB	TG	3-Chloro-1-propanol	S	Diethyl ether	S	NM	ppt
1,2-DBE	TG	3-Picoline	Crys.	DEG	S	P-xylene	ppt
2-Butanone	PG	4-Picoline	Crys.	Diisopropyl ether	S	Pyridine	S
1,2-DCB	TPG	Acetone	ppt	DMA	S	THF	ppt
1,3-DCB	TPG	Acetonitrile	ppt	DMF	S	Toluene	ppt
1,4-Dioxane	S	Benzene	S	DMSO	S	Water	ppt
1-Butanol	S	Benzyl alcohol	S	Ethanol	S		
1-Pentanol	S	Chlorobenzene	TPG	Ethyl acetate	S		
1-Propanol	S	Chloroform	TG	EG	S		
2-Butanol	PG	Cyclohexane	ppt	EGBE	S		
2-Ethyl pyridine	S	Cyclohexanone	S	Mesitylene	ppt		
2-Picoline	S	Cyclopentanone	S	Methanol	PG		
2-Propanol	TG	DCM	TG	NB	TPG	1% w/v	

Table 21. The gel screen results of **2.11** at 2% w/v in the presence of 0.5 equivalence of $CuCl_2$, it is clear that with the increase of **2.11** concentration, more gels formed.

$CuCl_2$	**0.5eq**	$CuCl_2$	**0.5eq**	$CuCl_2$	**0.5eq**	$CuCl_2$	**0.5eq**
1,2,4-TCB	TPG	3-Chloro-1-propanol	ppt	Diethyl ether	S	NM	ppt
1,2-DBE	TPG	3-Picoline	ppt	DEG	S	P-xylene	PG
2-Butanone	S	4-Picoline	S	Diisopropyl ether	S	Pyridine	S
1,2-DCB	G	Acetone	ppt	DMA	S	THF	PG
1,3-DCB	G	Acetonitrile	PG	DMF	S	Toluene	PG
1,4-Dioxane	S	Benzene	S	DMSO	S	Water	ppt
1-Butanol	PG	Benzyl alcohol	G	Ethanol	PG		
1-Pentanol	PG	Chlorobenzene	G	Ethyl acetate	S		
1-Propanol	ppt	Chloroform	ppt	EG	ppt		
2-Butanol	ppt	Cyclohexane	PG	EGBE	PG		
2-Ethyl pyridine	S	Cyclohexanone	ppt	Mesitylene	PG		
2-Picoline	S	Cyclopentanone	G	Methanol	G		
2-Propanol	TPG	DCM	ppt	NB	TG	2% w/v	

Table 22. The gel screen results of **2.11** at 1% w/v in the presence of 1.0 equivalence of $CuCl_2$, with the concentration of **2.11** keeping as a constant, the augment of the $CuCl_2$ metal solution did not make too much difference in gel screen test.

$CuCl_2$	**1.0eq**	**$CuCl_2$**	**1.0eq**	**$CuCl_2$**	**1.0eq**	**$CuCl_2$**	**1.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	S	NM	ppt
1,2-DBE	ppt	3-Picoline	ppt	DEG	S	P-xylene	ppt
2-Butanone	ppt	4-Picoline	ppt	Diisopropyl ether	S	Pyridine	S
1,2-DCB	TPG	Acetone	ppt	DMA	S	THF	PG
1,3-DCB	PG	Acetonitrile	ppt	DMF	S	Toluene	ppt
1,4-Dioxane	ppt	Benzene	ppt	DMSO	S	Water	ppt
1-Butanol	PG	Benzyl alcohol	S	Ethanol	PG		
1-Pentanol	PG	Chlorobenzene	TPG	Ethyl acetate	S		
1-Propanol	PG	Chloroform	G	EG	S		
2-Butanol	S	Cyclohexane	ppt	EGBE	ppt		
2-Ethyl pyridine	S	Cyclohexanone	PG	Mesitylene	ppt		
2-Picoline	PG	Cyclopentanone	PG	Methanol	PG		
2-Propanol	ppt	DCM	TPG	NB	TPG	1% w/v	

Table 23. The gel screen results of **2.11** at 2% w/v in the presence of 1.0 equivalence of $CuCl_2$, there even less solvents get gelled at this situation.

$CuCl_2$	**1.0eq**	$CuCl_2$	**1.0eq**	$CuCl_2$	**1.0eq**	$CuCl_2$	**1.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	ppt
1,2-DBE	ppt	3-Picoline	ppt	DEG	S	P-xylene	ppt
2-Butanone	S	4-Picoline	ppt	Diisopropyl ether	ppt	Pyridine	S
1,2-DCB	G	Acetone	ppt	DMA	S	THF	S
1,3-DCB	PG	Acetonitrile	S	DMF	S	Toluene	PG
1,4-Dioxane	PG	Benzene	PG	DMSO	S	Water	ppt
1-Butanol	ppt	Benzyl alcohol	G	Ethanol	PG		
1-Pentanol	PG	Chlorobenzene	ppt	Ethyl acetate	ppt		
1-Propanol	ppt	Chloroform	PG	EG	S		
2-Butanol	ppt	Cyclohexane	PG	EGBE	PG		
2-Ethyl pyridine	S	Cyclohexanone	TPG	Mesitylene	ppt		
2-Picoline	ppt	Cyclopentanone	S	Methanol	G		
2-Propanol	ppt	DCM	ppt	NB	TPG	2% w/v	

Table 24. The gel screen results of **2.11** at 1% w/v in the presence of 2.0 equivalence of $CuCl_2$, at this case, the least gels have been found and almost are partial gels.

$CuCl_2$	**2.0eq**	**$CuCl_2$**	**2.0eq**	**$CuCl_2$**	**2.0eq**	**$CuCl_2$**	**2.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	S
1,2-DBE	ppt	3-Picoline	S	DEG	S	P-xylene	ppt
2-Butanone	ppt	4-Picoline	ppt	Diisopropyl ether	ppt	Pyridine	S
1,2-DCB	S	Acetone	ppt	DMA	S	THF	PG
1,3-DCB	ppt	Acetonitrile	S	DMF	S	Toluene	ppt
1,4-Dioxane	S	Benzene	PG	DMSO	S	Water	ppt
1-Butanol	ppt	Benzyl alcohol	G	Ethanol	PG		
1-Pentanol	ppt	Chlorobenzene	ppt	Ethyl acetate	ppt		
1-Propanol	ppt	Chloroform	PG	EG	S		
2-Butanol	ppt	Cyclohexane	PG	EGBE	PG		
2-Ethyl pyridine	ppt	Cyclohexanone	PG	Mesitylene	ppt		
2-Picoline	ppt	Cyclopentanone	S	Methanol	ppt		
2-Propanol	ppt	DCM	S	NB	PG	1% w/v	

Table 25. The gel screen results of **2.11** at 2% w/v in the presence of 2.0 equivalence of $CuCl_2$, a little more partial gels have been discovered due to the more **2.11** have been added to the solution.

$CuCl_2$	**2.0eq**	$CuCl_2$	**2.0eq**	$CuCl_2$	**2.0eq**	$CuCl_2$	**2.0eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	ppt
1,2-DBE	ppt	3-Picoline	S	DEG	S	P-xylene	ppt
2-Butanone	ppt	4-Picoline	PG	Diisopropyl ether	ppt	Pyridine	Crys.
1,2-DCB	ppt	Acetone	PG	DMA	S	THF	PG
1,3-DCB	ppt	Acetonitrile	PG	DMF	S	Toluene	ppt
1,4-Dioxane	ppt	Benzene	ppt	DMSO	S	Water	ppt
1-Butanol	ppt	Benzyl alcohol	PG	Ethanol	PG		
1-Pentanol	ppt	Chlorobenzene	ppt	Ethyl acetate	ppt		
1-Propanol	ppt	Chloroform	PG	EG	S		
2-Butanol	ppt	Cyclohexane	PG	EGBE	PG		
2-Ethyl pyridine	ppt	Cyclohexanone	PG	Mesitylene	ppt		
2-Picoline	ppt	Cyclopentanone	S	Methanol	G		
2-Propanol	ppt	DCM	S	NB	PG	2% w/v	

Table 26. The gel screen results of **2.11** at 1% w/v in the presence of 0.5 equivalence of $Cu(NO_3)_2$ which shows the same with the result of $Cd(NO_3)_2$, only some of the solvents gelled.

$Cu(NO_3)_2$	**0.5eq**	$Cu(NO_3)_2$	**0.5eq**	$Cu(NO_3)_2$	**0.5eq**	$Cu(NO_3)_2$	**0.5eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	S
1,2-DBE	ppt	3-Picoline	S	DEG	S	P-xylene	S
2-Butanone	S	4-Picoline	S	Diisopropyl ether	S	Pyridine	S.
1,2-DCB	ppt	Acetone	S	DMA	S	THF	S
1,3-DCB	PG	Acetonitrile	ppt	DMF	S	Toluene	ppt
1,4-Dioxane	S	Benzene	PG	DMSO	S	Water	ppt
1-Butanol	S	Benzyl alcohol	ppt	Ethanol	S		
1-Pentanol	S	Chlorobenzene	PG	Ethyl acetate	S		
1-Propanol	S	Chloroform	ppt	EG	TG		
2-Butanol	S	Cyclohexane	ppt	EGBE	S		
2-Ethyl pyridine	S	Cyclohexanone	S	Mesitylene	S		
2-Picoline	ppt	Cyclopentanone	S	Methanol	PG		
2-Propanol	ppt	DCM	ppt	NB	S	1% w/v	

Table 27. The gel screen results of **2.11** at 2% w/v in the presence of 0.5 equivalence of $Cu(NO_3)_2$, only three partial gels gained from the test which indicates that aggrandizing the amount of **2.11** would even lower the gelation ability.

$Cu(NO_3)_2$	**0.5eq**	**$Cu(NO_3)_2$**	**0.5eq**	**$Cu(NO_3)_2$**	**0.5eq**	**$Cu(NO_3)_2$**	**0.5eq**
1,2,4-TCB	ppt	3-Chloro-1-propanol	S	Diethyl ether	ppt	NM	S
1,2-DBE	ppt	3-Picoline	S	DEG	PG	P-xylene	S
2-Butanone	ppt	4-Picoline	S	Diisopropyl ether	S	Pyridine	S.
1,2-DCB	ppt	Acetone	PG	DMA	S	THF	S
1,3-DCB	ppt	Acetonitrile	ppt	DMF	S	Toluene	ppt
1,4-Dioxane	S	Benzene	ppt	DMSO	S	Water	ppt
1-Butanol	ppt	Benzyl alcohol	ppt	Ethanol	PG		
1-Pentanol	ppt	Chlorobenzene	ppt	Ethyl acetate	S		
1-Propanol	S	Chloroform	ppt	EG	ppt		
2-Butanol	S	Cyclohexane	ppt	EGBE	S		
2-Ethyl pyridine	S	Cyclohexanone	S	Mesitylene	S		
2-Picoline	ppt	Cyclopentanone	S	Methanol	PG		
2-Propanol	ppt	DCM	ppt	NB	S	2% w/v	